PHILOSOPHICAL TRANSACTIONS.

I. The Bakerian Lecture.—*On the Diffusion of Liquids.*

By Thomas Graham, *F.R.S., F.C.S.*

ANY saline or other soluble substance, once liquefied and in a state of solution, is evidently spread or diffused uniformly through the mass of the solvent by a spontaneous process.

It has often been asked whether this process is of the nature of the diffusion of gases, but no satisfactory answer to the question appears to be obtained, owing, I believe, to the subject having been studied chiefly in the operations of endosmose, where the action of diffusion is complicated and obscured by the imbibing power of the membrane, which is peculiar for each soluble substance, but no way connected with the diffusibility of the substance in water. Hence also it was not the diffusion of the salt, but rather the diffusion of the solution, which was generally regarded. A diffusibility like that of gases, if it exists in liquids, should afford means for the separation and decomposition even of unequally diffusible substances, and being of a purely physical character, the necessary consequence and index of *density*, should present a scale of densities for substances in the state of solution, analogous to vapour densities, which would be new to molecular theory.

M. Gay-Lussac proceeds upon the assumed analogy of liquid to gaseous diffusion in the remarkable explanation which he suggests of the cold produced on diluting certain saline solutions, namely, that the molecules of the salt expand into the water like a compressed gas admitted into additional space.

The phenomena of solubility are at the same time considered by that acute philosopher as radically different from those of chemical affinity, and as the result of an attraction which is of a physical or mechanical kind. The characters indeed of these two attractions are strongly contrasted. Chemical combination is uniformly attended

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with the evolution of heat, while solution is marked with equal constancy by the production of cold. The substances which combine chemically are the dissimilar, while the soluble substance and its solvent are the like or analogous in composition and properties.

In the consideration of solubility, attention is generally engrossed entirely by the quantity of salt dissolved. But it is necessary to apprehend clearly another character of solution, namely, the degree of force with which the salt is held in solution, or the intensity of the solvent attraction, quite irrespective of quantity dissolved. In the two solid crystalline hydrates, pyrophosphate of soda and sulphate of soda, we see the same ten equivalents of water associated with both salts, but obviously united with unequal degrees of force, the one hydrate being persistent in dry air and the other highly efflorescent. So also in the solutions of two salts which are equally soluble in point of quantity, the intensity of the attraction between the salt and the water may be very different, as exemplified in the large but feeble solubility in water of such bodies as the iodide of starch or the sulphindylate of potash, compared with the solubility of hydrochloric acid or of the acetate of potash, which last two substances are capable of precipitating the two former, by displacing them in solution. Witness also the unequal action of animal charcoal in withdrawing different salts from solution, although the salts are equally soluble; and the unequal effect upon the boiling-point of water produced by dissolving in it the same weight of various salts. Besides being said to be small or great, the solubility of a substance has also therefore to be described as weak or strong.

The gradations of intensity observed in the solvent force are particularly referred to, because the inquiry may arise how far these gradations are dependent upon unequal diffusibility; whether indeed rapidity of diffusion is not a measure of the force in question.

I have only further to premise, that two views may be taken of the physical agency by which gaseous diffusion itself is effected, which are equally tenable, being both entirely sufficient to explain the phenomena.

On one theory, that of Dr. DALTON, the diffusibility of a gas is referred immediately to its elasticity. The same spring or self-repulsion of its particles which sends a gas into a vacuum, is supposed to propel it through and among the particles of a different gas.

The existence of an attraction of the particles of one gas for the particles of all other gases is assumed in the other theory. This attraction does not occasion any diminution of volume of gases on mixing, because it is an attraction residing on the surfaces of the gaseous molecules. It is of the same intensity for all gases, hence its effect in bringing about intermixture is dependent upon the weight of the molecules of the gases to be moved by it; and the velocity of diffusion of a gas comes to have the same relation to its density on this hypothesis as upon the other[*].

  [*] Both of the molecular theories of the diffusion of gases were first publicly explained, and at the same time ably discussed, with the reference to the law of diffusion which had been drawn from observation, by my late

The surface attraction of molecules assumed will recall the surface attraction of liquids, which is found necessary to account for the elevation of liquids in tubes and other phenomena of capillary attraction.

(1.) An early preliminary experiment was made upon the liquid diffusion of a body, with whose diffusion as a gas we are already well acquainted, namely, carbonic acid dissolved in water.

Two half-pound stoppered glass bottles were selected, of which the mouths were 1·2 inch in diameter, and the lips were ground flat so as to close tight when applied together (fig. 1). One of them, placed firmly in an upright position, was filled to the base of the neck with carbonic acid water. Over this distilled water was poured, care being taken to disturb the liquid below as little as possible, in filling up the neck. The second bottle, filled with distilled water and inverted upon a glass plate, was slipped over the first at the water-trough. The solution of carbonic acid in the lower bottle was thus placed in free communication by an aperture of 1·2 inch, with an equal volume of pure water in the upper bottle. It was expected that the carbonic acid would be found, in time, equally diffused through both bottles.

Fig. 1.
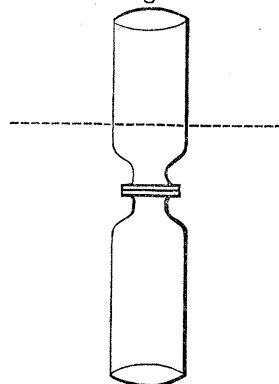
After forty-eight hours, the upper inverted bottle was again slipped off from the lower one, upon a glass plate, and the ratio of the gas found in the upper to that in the lower bottle determined by the weight of carbonate of baryta which the liquids of the two bottles afforded respectively. It was as 1·18 to 12·80 (about 1 to 11), instead of the ratio of equality, which would undoubtedly be the ultimate result of diffusion, were sufficient time allowed.

After five days, in a second experiment with a weaker solution of carbonic acid, the gas was found to be distributed—

In upper bottle . . . . 1·63
In lower bottle . . . . 8·44

or in the proportion of 1 to 5 nearly.

In other experiments where the liquid in the upper bottle was a solution in water of nitrous oxide gas, instead of pure water, the carbonic acid of the lower bottle was also observed to diffuse into the liquid above it, as freely as it did into pure water in a comparative experiment; the ultimate ratios being 1 to 0·12 in the nitrous oxide liquid, and 1 to 0·10 in the water experiment.

With the necks of the pair of bottles occupied by sponge charged with distilled water, the diffusion of the carbonic acid of the lower bottle proceeded with little

friend Mr. T. S. THOMSON of Clitheroe. A decided preference was given by Mr. THOMSON, and also by the late Mr. IVORY, to the last, or the attraction theory of diffusion, over that of gases being *vacua* to each other. See Phil. Mag., 3rd series, vol. xxv. pp. 51, 282.

change in its rapidity, or in the result when nitrous oxide was placed above it.   The carbonic acid found in the upper bottle, and which had diffused into it from the lower, was 0·231 when the upper bottle contained water alone, and 0·229 when it was water charged with three-fourths of its volume of nitrous oxide gas,—to 1 carbonic acid remaining undiffused in the lower bottle in both cases.

It appeared, then, that the liquid diffusion of carbonic acid was a slow process compared with its gaseous diffusion, quite as much as days are to minutes.

That this diffusion of the liquid carbonic acid takes place with undiminished vigour into water already saturated with nitrous oxide, the substance of all others most resembling carbonic acid in solubility and the whole range of its physical qualities. The diffusion of the liquid carbonic acid appears no more repressed by the liquid nitrous oxide, than the diffusion of gaseous carbonic acid is by gaseous nitrous oxide.

But the chief interest of these observations was the practical solution which they give to the question, whether, in conducting experiments on liquid diffusion, accidental causes of disturbance and intermixture of two liquids, communicating freely with each other, can be avoided.   It was made evident that little is to be feared from accidental dispersion when ordinary precautions are taken.

An excess of density in the lower liquid of not more than $\frac{1}{1000}$th part is found adequate to prevent any considerable change of place of the latter,—from expansion by heat, accidental tremors and such disturbing causes, which must exist,—for days together.

(2.) Another early inquiry was, how far is the diffusion of various salts governed or modified by the density of their solutions.

Solutions of eight hydrated acids and salts were prepared, having the common density of 1·200, and were set to diffuse into water in the following manner:—

Eighteen or twenty six-ounce phials were made use of to contain the solutions, and to form what I shall call the Solution phials or cells.   They were of the same make and selected from a large stock, of the common aperture of 1·175 inch.   Both the mouths and bottoms of these phials were ground flat.   The mode of making an experiment was first to fill the phial to the base of the neck, or rather to a constant distance of 0·6 inch below the ground surface of the lip.   A little disc of cork, provided with a slight upright peg of wood, was then floated upon the solution in the neck, after having been first dipt in water.   The neck itself was now filled up with pure water by means of a pointed sponge, the drop suspended from the sponge being made to touch the peg of the float, and water caused to flow in the gentlest manner, by slightly pressing the sponge.   The only other part of the apparatus, the Water-jar, was a plain cylindrical glass jar, of which the inner surface of the bottom was flat or slightly concave, to give a firm support to the phial.   The phial, with its solution only, was first placed in this jar partly filled with distilled water, and the neck of the former was then filled up with distilled water in this position, as before described, to avoid any subsequent movement.   The phial was ultimately entirely covered to the

depth of an inch with water, which required about 30 ounces of the latter, fig. 2. The saline solution in the diffusion cell or phial thus communicated freely with about 5 times its volume of pure water, the liquid atmosphere which invites diffusion. Another modification of this procedure was the substitution of phials cast in a mould, of the capacity of 4 ounces, or more nearly 2080 grs., which were ground down to a uniform height of 3·8 inches. The neck was 1·25 inch in diameter and 0·5 inch in depth; and the phial was filled up with the solution to be diffused to that point. The solution cell or phial and the water-jar form together a Diffusion cell.
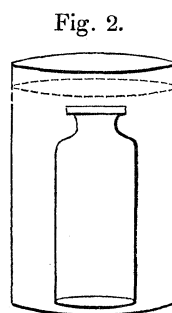
Fig. 2.

The diffusion was stopt, after twenty-seven days in the present experiments, by closing the mouth of the phial with a plate of glass, and then raising it out of the water-jar. The quantity of salt or of acid which had found its way into the water-jar,—the diffusion product as it may be called,—was then determined by evaporating to dryness for the salts, and by neutralizing the same liquid with a normal alkaline solution for the acids. The quantities of the acids diffused are estimated at present as protohydrates for the sake of comparison with the salts.

TABLE I.—Diffusion of Solutions of Density 1·200. Temp. 66° FAHR.

	Placed in solution cell.		Found in water-jar.	
	Proportion of anhydrous salt, or of acid protohydrate, to 100 of water.	Boiling-point.	Diffusion product.	
			In grains.	Ratio.
Chloride of sodium	34·21	225·5°	269·80	100
Nitric acid	37·93	227	581·20	215·42
Sulphuric acid	29·03	223	455·10	168·68
Chloride of potassium (density 1·178)...	34·86	221	320·30	118·71
Bisulphate of potash	31·85	216	319·00	118·23
Nitrate of soda	32·42	220	260·20	96·44
Sulphate of magnesia..............	22·38	214	95·87	35·53
Sulphate of copper................	21·56	213½	77·47	28·71

It appears that the diffusion from solutions of the same density is not equal but highly variable, ranging from 1 to 0·1333.

The results also favour the existence of a relation between large or rapid diffusibility and a high boiling-point. The latter property may be taken to indicate of itself a high degree of attraction between the salt and water.

I. CHARACTERS OF LIQUID DIFFUSION.

1. *Diffusion of Chloride of Sodium.*

The characters of liquid diffusion were first examined in detail in the case of this salt.

(1.) Do different proportions of chloride of sodium in solution give corresponding amounts of diffusion?

Solutions were prepared of chloride of sodium in the proportion of 100 water with 1, 2, 3 and 4 parts of the salt.

The diffusion of all the solutions was continued for the same time, eight days, at the mean temperature of 52°·5 FAHR.

Proportion of salt to 100 water.	Diffusion product.	
	In grains.	Ratio.
1	2·78	1·
2	5·54	1·99
3	8·37	3·01
4	11·11	4·00

The quantities diffused appear therefore to be closely in proportion (for this salt) to the quantity of salt in the diffusing solution. The density of the solutions containing 1, 2, 3 and 4 parts of chloride of sodium, was at 60°, 1·0067, 1·0142, 1·0213, 1·0285. The increase of density corresponds very nearly with the proportion of chloride of sodium in solution. A close approach to this direct relation is indeed observable in most salts, when dissolved in proportions not exceeding 4 or 5 per cent.

The relation which appears in these results is also favourable to the accuracy of the method of experimenting pursued. The variation from the speculative result does not in any observation exceed 1 per cent.

(2.) Is the quantity of salt diffused affected by temperature?

The diffusion of similar solutions of chloride of sodium was repeated at two new temperatures, 39°·6 and 67°, the one being above and the other below the preceding temperature. It was necessary to use artificial means to obtain the low temperature owing to the period of the season. A close box of double walls, namely, the ice-safe of the Wenham Ice Company, was employed, masses of ice being laid on the floor of the box, and the water-jars supported on a shelf above. The water and solution were first cooled separately for twenty-four hours in the ice-box, before the diffusion was commenced. It was found that the temperature could be maintained within a range of 2° or 3° for eight days. It was doubtful however whether the temperature was constantly the same to a degree or two in all the jars; and the results obtained at an artificial temperature were always less concordant and sensibly inferior in precision to observations made at the atmospheric temperature.

Diffusion of Chloride of Sodium.

Proportion of salt to 100 water.		Diffusion product.	
		In grains.	Ratio.
1	At 39°·6	2·63	1·
2	At 39°·6	5·27	2·00
3	At 39°·6	7·69	2·92
4	At 39·°6	10·00	3·80
1	At 67°	3·50	1·
2	At 67°	6·89	1·97
3	At 67°	9·90	2·83
4	At 67°	13·60	3·89

The proportionality in the diffusion is still well-preserved at the different tempe-
ratures. The deviations are indeed little, if at all, greater than might be occasioned
by errors of observation. The ratio of diffusion, for instance, from the solutions
containing 4 parts of salt, is 3·80 and 3·89 for the two temperatures, which numbers
fall little short of 4.

The diffusion manifestly increases with the temperature, and as far as can be
determined by three observations, in direct proportion to the temperature. The dif-
fusion-product from the 4 per cent. solution increases from 10 grs. to 13·60, with a
rise of temperature of 27°·4, or rather more than one-third. Supposing the same
progression continued, the diffusibility of chloride of sodium would be doubled by a
rise of 84 or 85 degrees.

(3.) The progress of the diffusion of chloride of sodium in such experiments as
have been narrated, was further studied by intercepting the operation after it had
proceeded for different periods of 2, 4, 6 and 8 days. The solution employed was
that containing 4 parts of salt to 100 water. Two of the six-ounce phials were dif-
fused at the same time for each period. The temperature given is the mean of the
temperatures of a water-jar observed each day of the period. The daily fluctuation
was not more than two or three-tenths of a degree FAHR.

In 2 days, temperature 63°·7; the salt diffused was 4·04 and 3·86 grs.; mean
3·95 grs.

In 4 days, temperature 63°·7; the salt diffused was 6·78 and 7·12 grs.; mean
6·95 grs.

In 6 days, temperature 63°·8; the salt diffused was 10·02 and 9·70 grs.; mean
9·86 grs.

In 8 days, temperature 64°; the salt diffused was 13·00 and 13·25 grs.; mean
13·12 grs.

The proportion diffused in the first period of two days is given directly in the first
experiments. The proper diffusion for each of the three latter periods of two days is
obtained by deducting from the result of each period the result of the period which
precedes it :—

Diffused in 1st two days . . . . . . 3·95 grs.
Diffused in 2nd two days . . . . . 3·00 grs.
Diffused in 3rd two days . . . . . . 2·91 grs.
Diffused in 4th two days . . . . . . 3·26 grs.

The diffusion appears to proceed pretty uniformly, if the amount diffused in the first period of two days be excepted. Each of the phials contained at first about 108 grs. of salt, of which the maximum quantity diffused is 13·12 grs. in eight days, or $\frac{1}{8·24}$ of the whole salt. Still the diffusion must necessarily follow a diminishing progression, which would be brought out by continuing the process for longer time, and appear at the earliest period in the salt of most rapid diffusion.

All the experiments which follow being made like the preceding on comparatively large volumes of solution in the phial, and for equally short periods of seven or eight days, may be looked upon as exhibiting pretty accurately the initial diffusion of such solutions, the influence of the diminishing progression being still small. The volume of water in the water-jar is also relatively so large, that the experiment approaches to the condition of diffusion into an Unlimited Atmosphere.

2. *Diffusion of various Salts and other Substances.*

With these notions regarding the influence of temperature and proportion of salt on the amount of diffusion, an examination was next undertaken of the relative diffusibility of a variety of salts and other substances. The results of this first survey I shall state as shortly as possible, as I consider these, as well as the experiments which preceded, as of a preliminary character. The experiments were all made by means of the diffusion phials already described, namely, the six-ounce phials, and with similar manipulations.

In the following experiments, the diffusion took place at a temperature ranging from 62° to 59°, mean 60°·5, and was continued for a period of eight days; the proportion of salt in solution to be diffused being always 20 salt to 100 water, or 1 to 5. I add as usual the density of the solutions.

TABLE II.—Diffusion of solutions of 20 salt to 100 water, at 60°·5, for eight days.

Name of salt.	Density of solution at 60°.	Anhydrous salt diffused.	
		In grains.	Means.
Chloride of sodium	1·1265·	58·5	
Chloride of sodium	1·1265	58·87	58·68
Sulphate of magnesia.................	1·185	27·42	27·42
Nitrate of soda	1·120	52·1	
Nitrate of soda	1·120	51·02	51·56
Sulphate of water	1·108	68·79	
Sulphate of water	1·108	69·86	69·32
Crystallized cane-sugar	1·070	26·74	26·74
Fused cane-sugar	1·066	26·21	26·21
Starch-sugar (glucose)	1·061	26·94	26·94
Treacle of cane-sugar	1·069	32·55	32·55
Gum-arabic	1·060	13·24	13·24
Albumen	1·053	3·08	3·08

The following additional ratios of diffusion were obtained from similar solutions at a somewhat lower temperature, namely 48°;—chloride of sodium 100, hydrate of potash 151·93, ammonia (from a 10 per cent. solution, saturated with chloride of sodium to increase its density) 70, alcohol (saturated with chloride of sodium) 75·74, chloride of calcium 71·23, acetate of lead 45·46.

Where two experiments upon the same salt are recorded in the table they are seen to correspond to within 1 part in 40, which may be considered as the limit of error in the present observations. It will be remarked that the diffusion of cane- and starch-sugar is sensibly equal, and double that of gum-arabic. On the other hand, the sugars have less than half the diffusibility of chloride of sodium. It is remarkable that the specifically lightest and densest solutions, those of the sugars and of sulphate of magnesia, approach each other closely in diffusibility. On comparing together, however, two substances of similar constitution, such as the two salts, chloride of sodium and sulphate of magnesia, that salt appears to be least diffusive of which the solution is densest.

But the most remarkable result is the diffusion of albumen, which is low out of all proportion when compared with saline bodies. The solution employed was the albumen of the egg, without dilution, but strained through calico and deprived of all vesicular matter. As this liquid, with a density of 1·041, contained only 14·69 parts of dry matter to 100 of water, the proportion diffused is increased in the table to that for 20 parts, to correspond with the other substances. In its natural alkaline state the albumen is least diffusive, but when neutralized by acetic acid, a slight precipitation takes place and the liquid filters more easily. The albumen is now sensibly more diffusive than before. Chloride of sodium appears 20 times more diffusible than albumen in the table, but the disparity is really greater; for nearly one-half of the matter which diffused consisted of inorganic salts. Indeed the experiment appears to promise a delicate method of proximate analysis peculiarly adapted for animal fluids. The value of this low diffusibility in retaining the serous or albuminous fluids within the blood-vessels at once suggests itself.

Similar results were obtained with egg albumen diluted and well-beaten with 1 and 2 volumes of water. The solution diluted with an equal bulk of water, and made slightly acid with acetic acid, contained 7½ dry matter to 100 water. Diffused from two four-ounce bottles of 1·25 inch aperture, for seven days, at a mean temperature of 43°·5 Fahr., it gave products of 1·73 and 1·48 gr., from the evaporation of two water-jars, in which cubic crystals of common salt were abundant. The whole matter thus diffused in two cells was found to consist of—

Coagulable albumen . . . . 0·94 gr.
Soluble salts . . . . 2·27 grs.
_____
3·21 grs.

The diffusion product of the same solution of albumen left alkaline, or without the

addition of acetic acid, in the same circumstances, was 1·41 and 1·20 grs. in two cells; and consisted of—

Coagulable albumen . . . . 0·63 gr.

Soluble salts . . . . 1·98 gr.

2·61 grs.

The diffusion product of a solution of 7½ parts of chloride of sodium to 100 water, from similar cells and for the same time and temperature, would amount to about 30 grs. of salt. It is to be remarked also that 5·53 grs. of the ignited salt diffused from albumen contained 1·32 gr. of potash or 23·9 per cent., which is a high proportion, and indicates that salts of potash diffuse out more freely from albumen than salts of soda.

Nor does albumen impair the diffusion of salts dissolved together with it in the same solution, although the liquid retains its viscosity. Three other substances, added separately in the proportion 5 parts to 100 of the undiluted solution of egg albumen, were found to diffuse out quite as freely from that liquid as they did from an equal volume of pure water: these were chloride of sodium, urea and sugar. Urea proved to be a highly diffusible substance. It nearly coincided in rate with chloride of sodium.

A second series of salts were diffused containing 1 part of salt to 10 of water; a smaller proportion of salt which admits of the comparison of a greater variety of salts. The temperature during the period of eight days was remarkably uniform, 60°—59°.

TABLE III.—Diffusion of solutions of 10 salt to 100 water at 59°·5.

Name of salt.	Density of solution at 60°.	Anhydrous salt diffused.	
		In grains.	Means.
Chloride of sodium......................	1·0668	32·3	
Chloride of sodium......................	1·0668	32·2	32·25
Nitrate of soda	1·0622	30·7	30·7
Chloride of potassium	1·0596	40·15	40·15
Chloride of ammonium	1·0280	40·20	40·20
Nitrate of potash	1·0589	35·1	
Nitrate of potash	1·0589	36·0	35·55
Nitrate of ammonia	1·0382	35·3	35·3
Iodide of potassium	1·0673	37·0	37·0
Chloride of barium	1·0858	27·0	27·0
Sulphate of water	1·0576	37·18	
Sulphate of water	1·0576	36·53	36·85
Sulphate of magnesia..................	1·0965	15·3	
Sulphate of magnesia..................	1·0965	15·6	15·45
Sulphate of zinc.....................	1·0984	15·6	
Sulphate of zinc.....................	1·0984	16·0	15·80

Before adverting to the relations in diffusibility which appear to exist between certain salts in the preceding table, I may state the results of the diffusion of the same solutions at a lower temperature.

TABLE IV.—Diffusion of solutions of 10 salt to 100 water at 37°·5.

Name of salt.	Anhydrous salt diffused.	
	In grains.	Means.
Chloride of sodium	22·21	
Chloride of sodium	22·74	22·47
Nitrate of soda	22·53	
Nitrate of soda	23·05	22·79
Chloride of ammonium	31·14	31·14
Nitrate of potash	28·84	
Nitrate of potash	28·56	28·70
Nitrate of ammonia	29·19	29·19
Iodide of potassium	28·10	28·10
Chloride of barium	21·42	21·42
Sulphate of water	31·11	
Sulphate of water	28·60	29·85
Sulphate of magnesia	13·03	
Sulphate of magnesia	13·11	13·07
Sulphate of zinc.......................	11·87	
Sulphate of zinc.......................	13·33	12·60

The near equality of the quantities diffused of certain isomorphous salts is striking at both temperatures. Chloride of potassium and chloride of ammonium give 40·15 and 40·20 grs. respectively in the first table. Nitrate of potash and nitrate of ammonia 35·55 (mean) and 35·3 grs. respectively in the first table, and 28·70 and 29·19 grs. in the second table. Sulphate of magnesia and sulphate of zinc 15·45 and 15·8 grs. (means) in the first table, with 13·07 and 12·60 grs. in the second. The relation observed is the more remarkable, that it is that of equal weights of the salts diffused, and not of atomically equivalent weights. In the salts of ammonia and potash, this equality of diffusion is exhibited also, notwithstanding considerable differences in density between their solutions; the density of the solution of chloride of ammonium, for instance, being 1·0280 and that of chloride of potassium 1·0596. It may have some relation however, but not a simple one, to the density of the solutions; sulphate of magnesia, of which the solution is most dense, being most slowly diffusive; and salts of soda being slower, as they are generally denser in solution, than the corresponding salts of potash. Nor does it depend upon equal solubility, for in none of the pairs is there any approach to equality in that respect.

A comparison was now made of the diffusibility of several acids. They were diffused from the same six-ounce phials, and for eight days. Solutions were prepared in the proportion of 4 parts of the anhydrous acid to 100 parts of water. The quantity of acid which diffused into the water-jar was estimated by the proportion of carbonate of soda which it neutralized.

TABLE V.—Diffusion of acid solutions (4 acid to 100 water) at 59°·3.

Name of acid.	Density of solution at 60°.	Anhydrous acid diffused.	
		In grains.	Means.
Nitric acid	1·0243	29·21 28·19	28·7
Hydrochloric acid	1·0225	34·22 33·99	34·1
Sulphuric acid	1·0317	18·71 18·26	18·48
Acetic acid............................	1·0094	19·13 17·19	18·16
Oxalic acid	1·0235	12·38 12·38	12·38
Arsenic acid	1·0320	12·16 12·16	12·16
Tartaric acid	1·0194	9·90 9·69	9·79
Phosphoric acid......................	1·0284	9·09 9·09	9·09
Chloride of sodium	1·0285	12·32	12·32

Considerable latitude thus appears to exist in the diffusibility of the different acids. To make the result for nitric acid fairly comparable with that for hydrochloric acid, the former should be increased in the proportion of 54 to 63, that is estimated as nitrate of water. This calculation gives 33·5 grs. of nitrate of water diffused, which approaches closely to 34·1 grs., the quantity for chloride of hydrogen or hydrochloric acid. The quantity of soda neutralized by the sulphuric and hydrochloric acids diffused was as 14·32 to 28·97, or nearly as 1 to 2. Sulphuric and acetic acids, on the other hand, appear to be equally diffusible. Phosphoric acid is the least diffusible acid in the series, presenting only about half the diffusion product of the two last-mentioned acids. The solution of phosphoric acid had been boiled for half an hour before diffusion, and was therefore in the tribasic state. The same precaution was not thought of for arsenic acid, although it is possibly required by this acid also. These two acids do not exhibit the equality of diffusion anticipated from their recognized isomorphism, but it is to be stated that the acidimetrical method of analysis followed is not so properly applicable to these two acids as it is to all the others.

3. *Diffusion of Ammoniated Salts of Copper.*

It was interesting to compare together such related salts as sulphate of copper, the ammoniated sulphate of copper or soluble compound of sulphate of copper with 2 equivs. of ammonia and the sulphate of ammonia. It is well known that metallic oxides, or subsalts of metallic oxides, when dissolved in ammonia or the fixed alkalies, are easily taken down by animal charcoal. This does not happen with the ordinary neutral salts of the same acids, which are held in solution by a strong attraction. Supposing the existence of a scale of the solvent attraction of water, the preponderance of the charcoal attraction will mark a term in that scale. And if the solvent

force is nothing more than the diffusive tendency, it will follow that salts which can be taken down by charcoal must be less diffusible than those which cannot.

Of sulphate of ammonia and sulphate of copper, solutions were prepared, consisting of 4 anhydrous salt to 100 water, the sulphate of ammonia being of course taken as $NH_4O . SO_3$. The solution of the copper salt was divided into two portions, one of which had caustic ammonia added to it in slight excess, so as to produce the azure blue solution of ammonio-sulphate of copper.

The solutions were diffused for eight days, at a mean temperature of $64°\cdot9$ for the sulphates and nitrates, and $67°\cdot7$ for the chlorides.

TABLE VI.—Diffusion of solutions, 4 salt to 100 water.

Name of salt.	Density of solution at temperature of experiment.	Anhydrous salt diffused in grains.
Sulphate of ammonia.................	1·0235	12·13
Sulphate of ammonia.................	1·0235	11·96
Sulphate of copper	1·0369	6·19
Sulphate of copper	1·0369	6·51
Ammonio-sulphate of copper	1·0308	1·45
Ammonio-sulphate of copper	1·0308	1·43
Nitrate of ammonia	1·0136	16·15
Nitrate of ammonia	1·0136	15·44
Nitrate of copper	1·0323	9·77
Nitrate of copper	1·0323	9·77
Ammonio-nitrate of copper	1·0228	1·77
Ammonio-nitrate of copper	1·0228	1·36
Chloride of ammonium..............	1·0100	16·18
Chloride of ammonium..............	1·0100	17·00
Chloride of copper	1·0328	10·83
Chloride of copper	1·0328	10·48
Ammonio-chloride of copper	1·0209	4·54
Ammonio-chloride of copper	1·0209	3·94

It is to be observed, that in preparing the ammoniated salts, the solutions of the neutral salts of copper were slightly diluted by the water of the solution of ammonia added to them, so that the proportion of salt of copper which they possessed was sensibly reduced below 4 per cent. On the other hand, the copper salt which diffused out is estimated, not as ammoniated, but as neutral salt. It will be observed that the quantity of sulphate of copper diffused out in the experiments falls from 6·35 in the neutral salt to 1·44 gr. in the ammoniated salt; of nitrate of copper from 9·77 to 1·56, and of chloride of copper from 10·65 to 4·24. These numbers are to be taken only as approximations; they are sufficient however to prove a much reduced diffusibility in the ammoniated salts of copper.

It will be remarked that the nitrate of ammonia and chloride of ammonium approximate, 15·80 and 16·59 grs.; as do also the nitrate and chloride of copper, 9·77 and 10·65 grs.; the chlorides, which were diffused at the higher temperature by $2°\cdot8$, exceeding the nitrates in both cases.

4. *Diffusion of Mixed Salts.*

When two salts can be mixed without combining, it is to be expected that they will diffuse separately and independently of each other, each salt following its special rate of diffusion.

(1.) Anhydrous sulphate of magnesia and sulphate of water (oil of vitriol), one part of each, were dissolved together in 10 parts of water, and the solution allowed to diffuse for four days at 61°·5.

The water-jar was found to have acquired—

<div style="text-align:center">

Sulphate of magnesia . . .   5·60 grs.

Sulphate of water   . . . .   21·92 grs.

_____

27·52 grs.

</div>

The experiment with the same diffusion cell and liquid being continued for a second period, this time of eight days, there was found to be simultaneously diffused, of—

<div style="text-align:center">

Sulphate of magnesia . . .   9·46 grs.

Sulphate of water   . . . .   29·32 grs.

_____

38·78 grs.

</div>

It is obvious that the inequality should be greatest in the first period of diffusion, or with the initial diffusion, as it actually appears above, and become less and less sensible as the proportion of the low diffusive salt comes to be increased in the solution phial.

In former experiments upon the solution of sulphate of magnesia alone in water, as 1 salt to 10 water, compared with sulphate of water, also as 1 to 10, the disparity in the diffusion of these two salts was less considerable, being only as 1 to 2·385, instead of 1 to 3 or 4.

(2.) A solution was also diffused of 1 part of anhydrous sulphate of soda and 1 part of chloride of sodium in 10 parts of water, for four days at 61°·5. The salt which diffused out in that time consisted of—

<div style="text-align:center">

Sulphate of soda . . . . .   9·48 grs.

Chloride of sodium . . .   17·80 grs.

_____

27·28 grs.

</div>

The sulphate of soda in the last experiment had begun to crystallize in the solution phial, from a slight fall of temperature, before the diffusion was interrupted, a circumstance which may have contributed to increase the inequality of the proportions diffused of these two salts.

(3.) A solution of equal weights of anhydrous carbonate of soda and chloride of sodium, namely, of 4 parts of the one salt and 4 parts of the other, to 100 water, was diffused from 3 four-ounce phials of 1·25 inch aperture, at a mean temperature of 57°·9 and for seven days. The diffusion product amounted to 17·10, 17·58 and 18·13 grs.

of mixed salt in the three experiments. The analysis of the last product of 18·13 grs. gave—

Carbonate of soda	5·68	31·33
Chloride of sodium	12·45	68·67
	18·13	100·00

Here the carbonate of soda presents a diffusion less than one-half of that of chloride of sodium. The difference is again greater than the peculiar diffusibilities of the same salts as they appear when the salts are separately diffused. For in experiments made in the same phials with solutions of 4 parts of each salt singly to 100 water, but with a lower temperature by 3°·6, namely, at 54°·3, the diffusion product of the carbonate of soda was 7·17 and 7·34 grs. in two experiments, of which the mean is 7·25 grs.; while the diffusion product of the chloride of sodium was 11·18 and 10·73 grs. in two experiments, of which the mean is 10·95 grs. The quantity of chloride of sodium diffused being taken at 100 in both sets of experiments, we have diffused—

Of carbonate of soda 66·18, when diffused singly.

Of carbonate of soda 45·64, when diffused with chloride of sodium.

The least soluble of the two salts appears in all cases to have its diffusibility lessened in the mixed state. The tendency to crystallization of the least soluble salt must evidently be increased by the admixture. Now it is this tendency, or perhaps more generally the increased attraction of the particles of a salt for each other, when approximated by concentration, which most resists the diffusion of a salt, and appears to weaken the diffusive force in mixtures, as it is also found to do so in a strong solution of a single salt.

(4.) Equal weights of nitrates of potash and ammonia dissolved, as in certain preceding experiments, in five times the weight of the mixed salts of water, and diffused for eight days, gave in two experiments—

	At 59°·4.	At 52°·6.
Nitrate of potash	28·39	25·88
Nitrate of ammonia	36·16	30·36
	64·55	56·24

The inequality in the diffusion of these two nitrates is singular, considering that in solutions of 1 salt to 10 water, they appeared before to be equally diffusive. But on now comparing the diffusion of solutions of 1 salt to 5 water, at 52°·6, the salts no longer diffused in equal proportions:—

Nitrate of potash gave . . . . 57·93 grs.

Nitrate of ammonia gave . . . . 82·08 grs.

The solution of nitrate of potash last diffused was nearly a saturated one, while that of nitrate of ammonia is far from being so. The first has its diffusibility, in consequence, impaired, and falls considerably below the second.

The relatively diminished diffusibility of sulphate of magnesia, when associated with sulphate of water, is probably connected with a similar circumstance; sulphate of magnesia being less soluble in dilute sulphuric acid than in pure water.

(5.) The salt which diffused from a strong solution of sulphates of zinc and magnesia, consisting of 1 part of each of these salts in the anhydrous state and 6 parts of water, did not consist of the two salts in exactly equal proportions. The mixture of salts, diffused for eight days, as in the late experiments, gave the following results:—

	Exp. I.	II.	III.
Sulphate of zinc	8·12	7·49	8·12
Sulphate of magnesia	8·68	8·60	8·75
	16·80	16·09	16·87

There is therefore always a slight but decided preponderance of sulphate of magnesia, the more soluble salt, in the diffusion product. These last experiments were made at an early period with another object in view, namely, to ascertain whether in closely related salts, such as the present sulphates of magnesia and zinc, the two salts might be elastic to each other, like the particles of one and the same salt, so that one salt might possibly suppress the diffusion of the other, and diffuse alone for both. The experiments lend no support to such an idea.

It appears from all the preceding experiments, that the inequality of diffusion which existed, is not diminished but exaggerated in mixtures, a curious circumstance, which has also been observed of mixed gases.

5. *Separation of Salts of different Bases by Diffusion.*

It was now evident that inequality of diffusion supplies a method for the separation, to a certain extent, of some salts from each other, analogous in principle to the separation of unequally volatile substances by the process of distillation. The potash salts appearing to be always more diffusive than the corresponding soda salts, it follows, that if a mixed solution of two such salts be placed in the solution phial, the potash salt should escape into the water atmosphere in largest proportion, and the soda salt be relatively concentrated in the phial. This anticipation was fully verified.

(1.) A solution was prepared of equal parts of the anhydrous carbonates of potash and soda in 5 times the weight of the mixture of water. Diffused from a small thousand-grain phial of 1·1 inch aperture, into 6 ounces of water, for nineteen days, at a temperature above 60°, it gave a liquid of density 1·0350, containing a considerable quantity of the salts. Of these mixed salts, converted into chlorides by the addition of hydrochloric acid, 9·39 grs., being treated with bichloride of platinum in the usual manner, gave 19·39 grs. of the double chloride of platinum and potassium, equivalent to 5·91 grs. of chloride of potassium; and left in solution 3·44 grs. of chloride of sodium: loss 0·04 gr. These chlorides represent 5·46 grs. of carbonate of potash and

3·12 grs. of carbonate of soda. The salts actually diffused out were therefore in the proportion of—

Carbonate of soda. . . . . 36·37
Carbonate of potash . . . . 63·63
——————
100·00

(2.) In another similar experiment from a six-ounce phial into $8\frac{1}{2}$ ounces of water, the liquid of the water-jar, after twenty-five days' diffusion, contained the two carbonates in nearly the same proportions as before, namely—

Carbonate of soda . . . . 35·2
Carbonate of potash . . . . 64·8
——————
100·0

(3.) A partial separation of the salts of sea-water was effected in a similar manner.

The sea-water (from Brighton) was of density 1·0265. One thousand grs. of the liquid yielded 35·50 grs. of dry salts, of which 2·165 grs. were magnesia. The dry salts contain therefore 6·10 per cent. of that earth.

Six thousand-grain phials, of 1·1 inch aperture, were properly filled with the sea-water and placed in six tumblers, each of the last containing 6 ounces of water. Temperature about 50°. The diffusion was interrupted after eight days. The salts of the sea-water were now found to be divided as follows :—

Diffused into the tumblers . . . . 92·9 grs., or 36·57 per cent.
Remaining in the phials . . . . . 161·1 grs., or 63·43 per cent.
——————   ——————
254·0   100·00

Rather more than one-third of the salts has therefore been transferred from the solution phials to the water-jars by diffusion.

Of the diffused salts in the tumblers, 46·5 grs. were found to contain 1·90 gr. magnesia, or 4·09 per cent. Hence we have the following result :—

Magnesia originally in salts of sea-water . . . 6·01 per cent.
Magnesia in salts diffused from sea-water . . . 4·09 per cent.

The magnesia, also, must in consequence be relatively concentrated in the liquid remaining behind in the diffusion cells.

A probable explanation may be drawn from the last results of the remarkable discordance in the analysis of the waters of the Dead Sea, made by different chemists of eminence. I refer to the relative proportion of the salts, and not their absolute quantity, the last necessarily varying with the state of dilution of the saline water when taken up. The lake in question falls in level 10 or 12 feet every year, by evaporation. A sheet of fresh water of that depth is thrown over the lake in the wet season, which water may be supposed to flow over a fluid nearly 1·2 in density, without greatly disturbing it. The salts rise from below into the superior stratum

by the diffusive process, which will bring up salts of the alkalies with more rapidity than salts of the earth, and chlorides, of either class, more rapidly than sulphates. The composition of water near the surface must therefore vary greatly, as this process is more or less advanced.

(4.) I may be allowed to add another experiment which is curious for the protracted immobility of a column of water which it exhibits, as well as for the separation occurring, which last may be interesting also in a geological point of view. A plain glass cylinder with a foot, 11 inches in height, and of which the capacity was 64 cubic inches, had 8 cubic inches poured into it of a saturated solution of carbonate of lime in carbonic acid water, containing also 200 grs. of chloride of sodium dissolved. Distilled water was then carefully poured over the saline solution, so as to fill up the jar, a float being used and the liquid disturbed as little as possible in the operation. The mouth of the jar was lastly closed by a ground glass plate, and it was left undisturbed upon the mantelpiece of a room without a fire, from March 20 to September 24 of the present year, or for six months and four days. Afterwards, on removing the cover, the fluid was observed not to have evaporated sensibly, and it exhibited no visible deposit. This I was not surprised at, as no deposit appeared in a similar experiment with the jar uncovered, after the lapse of six weeks. The liquid in the former jar was now carefully drawn off by a small siphon with the extremity of both its limbs recurved so as to open upwards, in four equal portions, which may be numbered from above downwards. Equal quantities of the four strata of liquids gave the following proportions of chloride of sodium and carbonate of lime :—

	Chloride of sodium.	Carbonate of lime.
No. 1.	21·91	0·10
No. 2.	23·41	0·22
No. 3.	23·55	0·38
No. 4.	23·99	0·42

The diffusion of the chloride of sodium has therefore not yet reached complete uniformity, although approaching it, the proportion of that salt obtained from the top and bottom strata being as 11 to 12. But the diffusion of the carbonate of lime appears much less advanced, the proportion of that substance being as 1 to 4 at the top and bottom of the liquid column. The slight difference in density of the strata, it may be further remarked, must have been sufficient to preserve such a column of liquid entirely quiescent, as shown by the distribution of the carbonate of lime, during the considerable changes of temperature of the season.

Chemical analysis, which gives with accuracy the proportions of acids and bases in a solution, furnishes no means of deciding how these acids and bases are combined, or what salts exist in solution. But it is possible that light may be thrown on the constitution of mixed salts, at least when they are of unequal diffusibility, by means of a diffusion experiment. With reference to sea-water, for instance, it has been a question in what form the magnesia exists, as chloride or as sulphate; or how much

exists in the one form and how much in the other. Knowing however the different rates of diffusibility of these two salts, which is nearly chloride 2 and sulphate 1, and their relation to the diffusibility of chloride of sodium, we should be able to judge from the proportion in which the magnesia travels in company with chloride of sodium, whether it is travelling in the large proportion of chloride of magnesium, in the small proportion of sulphate of magnesia, or in the intermediate proportion of a certain mixture of chloride and sulphate of magnesia. But here we are met by a difficulty. Do the chloride of magnesium and sulphate of magnesia necessarily pre-exist in sea-water in the proportions in which they are found to diffuse? May not the more easy diffusion of chlorides determine their formation in the diffusive act, just as evaporation determines the formation of a volatile salt—producing carbonate of ammonia, for instance, from hydrochlorate of ammonia with carbonate of lime in the same solution? We shall see immediately that liquid diffusion, as well as gaseous evaporation, can produce chemical decompositions.

6. *Decomposition of Salts by Diffusion.*

(1.) At an early period of the inquiry, a solution was diffused of bisulphate of potash, saturated at 68° and of density 1·280, from the six-ounce phial of 1·175 inch aperture, into 20 ounces of water. The period of diffusion extended to fifty days. About the middle of that period, a few small crystals of sulphate of potash, amounting probably to 3 or 4 hundredths of a grain, appeared in the diffusion cell and never afterwards dissolved away. When terminated, the liquid remaining in the solution cell was found of density 1·154; that in the water-jar 1·0326. A portion of the latter liquid gave by analysis—

Sulphate of potash	20·37	} Bisulphate of potash.
Sulphate of water	11·47	
Sulphate of water	12·77	
	44·61	

It thus appears that the bisulphate of potash undergoes decomposition in diffusing, and that the acid diffuses away to about double the extent, in equivalents, of the sulphate of potash. This greater escape of the acid will also account for the deposition of crystals of the neutral sulphate in the solution cell.

(2.) A similar experiment was made with another double sulphate of greater stability, common potash-alum. The solution of 4 anhydrous alum in 100 water, was diffused from the six-ounce phial into 24 ounces of water, at 64°·2, for eight days. The quantity of salt diffused in that time amounted only to 7·48 grs. It contained 1·06 gr. alumina, which is equivalent to 5·33 grs. of alum. The diffused salt gave off no acid vapours at 600°. We may therefore suppose the excess of salt which is diffused to be sulphate of potash. The diffusion product of alum, at 64°, appears to be—

Alum	5·33	71·26
Sulphate of potash . . .	2·15	28·74
	7·48	100·00

In a second experiment, the diffusion product amounted to 6·39 grs., of which 0·95 gr. was alumina; and it is represented by 4·77 alum and 1·52 sulphate of potash.

In connexion with the low diffusibility of the sulphate of alumina of alum, it was found that the addition of caustic potash to the alum solution, so as to convert it into an aluminate of potash, increased the diffusibility of the alumina. The diffusion product from the 4 per cent. solution of alum so treated contained 1·62 gr. of alumina in one experiment and 1·54 in another.

As alum is a salt of great stability, it presents a severe test of the influence in question. The decomposition of this double salt by diffusion was further confirmed therefore in experiments made by means of the four-ounce diffusion phials of 1·25 inch aperture, and the alteration which the salt undergoes in the process more exactly ascertained. The experiments were made at a mean temperature of 57°·9, and lasted seven days; the solution employed being of 4 anhydrous alum to 100 water, as before.

In three experiments, the salt diffused out amounted to 5·73, 5·80 and 5·65 grs.; of which the mean is 5·73 grs. The latter quantity gave 0·82 alumina and 3·22 sulphuric acid, which correspond to 4·11 anhydrous alum and 1·62 neutral sulphate of potash. Or, we have as the diffusion product of alum, in 100 parts—

Alum . . . . 71·73
Sulphate of potash . . . . 28·27
                                    ————
                                    100·00

This analysis corresponds closely with the diffusion product of the former experiments, which gave 71·26 per cent. of alum. The solution of alum which remains behind in the solution phials must of course acquire an excess of sulphate of alumina.

The salt, sulphate of alumina, did not appear to be decomposed when diffused alone. A four per cent. solution of the hydrated sulphate of alumina, which is manufactured at Newcastle, when diffused in the same circumstances as the preceding solutions of alum, gave 3·40 grs. of anhydrous sulphate of alumina, in which the acid was to the alumina as 2·95 equivalents of the former to 1 equivalent of the latter, or as nearly as possible in the proportion of 3 equivalents of acid to 1 of base. As the Newcastle salt contained almost exactly half its weight of water, the 3·40 grs. of anhydrous salt diffused out are equivalent to 6·80 grs. of hydrated sulphate of alumina. The sulphate of alumina appears thus to be more diffusive than the double sulphate of alumina and potash, in the proportion of 6·80 to 5·73.

(3.) It was interesting to observe what really diffuses from the ammoniated sulphate of copper ($CuO, SO_3, 2NH_3 + HO$), and to find if the low diffusibility of that salt is attended with decomposition. The diffusion of the ammoniated sulphate of copper was therefore repeated from a 4 per cent. solution in the six-ounce solution phial, for eight days, at 64°·2. In evaporating the water of the jar afterwards, the ammoniated sulphate of copper present was necessarily decomposed, by the escape of ammonia, and a subsulphate of copper precipitated. The copper found, however, was

estimated as neutral sulphate of copper.   The diffusion product of two experiments may be represented as follows, in grains:—

	I.	II.
Sulphate of copper	0·81	0·97
Sulphate of ammonia	5·46	5·53
	6·27	6·50

The abundant formation and separation of sulphate of ammonia in these experiments, prove that the ammoniated sulphate of copper is largely decomposed in diffusion.

(4.) Perhaps the most interesting result of this kind is a solution which is given of the problem of the decomposition of the alkaline sulphates by means of lime.

Solutions were prepared of $\frac{1}{2}$ per cent. of sulphate of potash and of chlorides of potassium and sodium in lime-water.   Two solution phials were filled with each of these solutions, and placed for diffusion in water-jars filled with lime-water, at 49°, for seven days.

In the sulphate no deposition of crystallized sulphate of lime took place within the solution phial, while the water-jar acquired an alkaline reaction, which remained after precipitating the lime entirely by carbonic acid gas and evaporating twice to dryness.   Hydrate of potash, it will afterwards appear, is an eminently diffusive salt, having double the diffusibility of sulphate of potash.   The tendency of the former to diffuse enables the affinity of the lime for sulphuric acid to prevail, and the alkali is liberated and diffused away into the external atmosphere of lime-water.   By the latter, hydrate of lime is returned to the solution cell and the decomposition continued.   The salt diffused in the two cells amounted to 2·60 grs., of which 0·62 gr., or 23·85 per cent., was hydrate of potash.   The chlorides of potassium and sodium, on the contrary, were not sensibly decomposed.

It is known that a precipitation of sulphate of lime may occur, with a larger proportion of sulphate of potash in lime-water, in a close phial without external diffusion. As the decomposition of the sulphate of potash, in the latter case, has been referred to the insolubility of the sulphate of lime, so the decomposition in the former circumstances is referred, in a similar sense, to the high diffusibility of hydrate of potash.

7. Diffusion of Double Salts.

How is the diffusion of two salts affected by their condition of combination as a double salt?   A solution of the double sulphate of magnesia and potash, in the proportion of 100 water to 4 anhydrous salt, was operated upon in the four-ounce diffusion phials of 1·25 inch aperture, with a period of diffusion of seven days, at 57°·9 FAHR.   The diffusion product of the double salt was 8·09 and 7·81 grs. in two experiments: mean, 7·95 grs.

The constituent salts, sulphate of magnesia and sulphate of potash, were now dis-

solved separately, in the proportions in which they existed in the double salt, namely, 1·65 gr. anhydrous sulphate of magnesia in 100 water, and 2·35 grs. sulphate of potash in 100 water, making up together 4 parts of salts. The two solutions thus contain equivalent quantities of the different sulphates.

The separate diffusion of the sulphate of magnesia was 2·09, 2·11 and 2·40 grs. in three cells; and of the sulphate of potash, 5·83, 5·97 and 5·54 grs. in three cells; the circumstances of the experiments being the same as those of the double salt. The means of the two salts are 2·20 and 5·78 grs.; and the sum of the two means 7·98 grs. The result is, that the separate diffusion of the constituent salts is almost identical with their diffusion when combined as a double salt:—

Diffusion of the double sulphate of magnesia and potash . . . 7·95 grs.

Diffusion of equivalents of sulphate of magnesia and sulphate of potash in separate cells . . . . } 7·98 grs.

It would thus appear that the diffusibility of this double salt is the sum of the separate diffusions of its constituent salts.

It has been a question whether a double salt is formed at once when its constituent salts are dissolved together, or not till the act of crystallization of the compound salt. Equivalents of the same two sulphates, making up 4 parts, were dissolved together without heat in 100 water. Now the diffusion from this mixture, which has the composition of the preceding solution of the double salt, exhibited notwithstanding a sensibly different result of diffusion, giving 7·28, 7·37 and 7·26 grs. in three cells mean, 7·30 grs. The diffusion of the double salt was greater, namely, 7·95 grs. Hence a strong presumption that the mixed salts last diffused were not combined, and that the double sulphate of magnesia and potash is not necessarily formed immediately upon dissolving together its constituent salts.

In early experiments of a similar nature made upon the double salt, sulphate of copper and potash, and upon a mixture of the two sulphates newly dissolved together, a similar result was obtained. While the diffusion of the mixed salts was 25·6 grs., that of the same weight of the combined salts (the double sulphate) was 30 grs. The double salt appears more diffusible, in both cases, than its mixed constituents.

These double salts appear to dissolve in water without decomposition, although the single salts may meet in solution without combining. Hence in a mixture of salts we may have more than one state of equilibrium possible. And when a salt, like alum, happens to be dissolved in such a way as to decompose it, the constituents are not necessarily reunited by subsequent mixing. Many practices in the chemical arts, which seem empirical, have their foundation possibly in facts of this kind.

8. *Diffusion of one Salt into the Solution of another Salt.*

It was curious and peculiarly important, in reference to the relation of liquid to gaseous diffusion, to find whether one salt A would diffuse into water already charged

with an equal or greater quantity of another salt B, as a gas a freely diffuses into the space already occupied by another gas b; the gas b in return diffusing at the same time into the space occupied by a. Or whether, on the contrary, the diffusion of the salt A is resisted by B. The latter result would indicate a neutralization of the water's attraction, and a kind of equivalency or equality of power and exchangeability of different salts, in respect of that effect, which would divide entirely the phenomena of liquid from those of gaseous diffusion.

(1.) A solution of 4 parts of carbonate of soda to 100 water, of density 1·0406, was placed in the six-ounce diffusion phial of 1·175 inch aperture, and allowed to communicate with 24 ounces of water.

Two similar diffusion phials, equally charged, were immersed in 24 ounces of a solution of 4 parts of chloride of sodium to 100 water, having the density 1·0282. The diffusion proceeded for eight days, in all cases, at 64°. The proportion of carbonate of soda found without in the water-jar afterwards, was ascertained by an alkalimetrical process, the neutralization being effected at the boiling-point. The following are the results :—

Experiment   I. Diffusion product into water. . .   9·06 grs. of carbonate of soda.

Experiment II. Diffusion product into solution of chloride of sodium . . . . } 8·82 grs. of carbonate of soda.

Experiment III. Diffusion product into solution of chloride of sodium . . . . } 9·10 grs. of carbonate of soda.

It thus appears that 4 per cent. of chloride of sodium present in the water atmosphere of the jar has no sensible effect in retarding the diffusion into it, from the solution cell, of carbonate of soda from a solution containing also 4 per cent. of the latter.

(2.) The experiment was varied by allowing the solution of carbonate of soda to diffuse into a solution of sulphate of soda, a salt more similar to the former in solubility and composition. The solution of the latter, containing 4 per cent., was of density 1·0352. The temperature and period of diffusion were the same as before:—

Experiment IV. Diffusion product into solution of sulphate of soda . . . . } 7·84 grs. of carbonate of soda.

Experiment V. Diffusion product into solution of sulphate of soda . . . . } 7·82 grs. of carbonate of soda.

Here we find a small reduction in the quantity of carbonate of soda diffused, amounting to one-eighth of the whole. The sulphate of soda has therefore exercised a positive interference in checking the diffusion of the carbonate to that extent. So small and disproportionate an effect however is scarcely sufficient to establish the existence of a mutual elasticity and resistance between these two salts.

Still it might be said, may not the diffusion of one salt be resisted by another salt which is strictly isomorphous with the first?

(3.) A solution of 4 parts of nitrate of potash to 100 of water, of density 1·0241, placed in the solution phial, was allowed to communicate with water containing 4 per cent. of nitrate of ammonia in the water-jar, which last solution was of density 1·0136; with all other circumstances as before. With one solution phial having the usual aperture, 1·175 inch, the diffusion product was 15·32 grs. of nitrate of potash. With a second phial, having a larger aperture of 1·190 inch, the diffusion product was 18·03 grs. of nitrate of potash. No comparative experiment, on the diffusion of nitrate of potash into water, was made at the same time. But nitrate of ammonia, which appeared before to coincide in diffusibility with nitrate of potash, gave on a former occasion, in similar circumstances, and at 64°·9, nearly the same temperature, a diffusion product of 15·80 grs. The quantity of nitrate of potash (15·32 grs.) which diffused into the solution of nitrate of ammonia approaches so closely to the number quoted, that we may safely conclude that the diffusion of nitrate of potash is not sensibly resisted by nitrate of ammonia, although these two salts are closely isomorphous. They are still therefore inelastic to each other, like two different gases.

These experiments have been made upon dilute solutions, and it is not at all impossible that the result may be greatly modified in concentrated solutions of the same salts, or when the solutions approach to saturation. But there is reason to apprehend that the phenomena of liquid diffusion are exhibited in the simplest form by dilute solutions, and that concentration of the dissolved salt, like compression of a gas, is attended often with a departure from the normal character.

On approaching the degree of pressure which occasions the liquefaction of a gas, an attraction appears to be brought into play, which impairs the elasticity of the gas; so on approaching the point of saturation of a salt, an attraction of the salt molecules for each other, tending to produce crystallization, comes into action, which will interfere with and diminish that elasticity or dispersive tendency of the dissolved salt which occasions its diffusion.

We are perhaps justified in extending the analogy a step further between the characters of a gas near its point of liquefaction and the conditions which we may assign to solutions. The theoretical density of a liquefiable gas may be completely disguised under great pressure. Thus, under a reduction by pressure of 20 volumes into 1, while the elasticity of air is 19·72 atmospheres, that of carbonic acid is only 16·70 atmospheres, and the deviation from their normal densities is in the inverse proportion. Of salts in solution the densities may be affected by similar causes, so that although different salts in solution really admit of certain normal relations in density, these relations may be concealed and not directly observable.

The analogy of liquid diffusion to gaseous diffusion and vaporization is borne out in every character of the former which has been examined. Mixed salts appear to diffuse independently of each other, like mixed gases, and into a water atmosphere already charged with another salt as into pure water. Salts also are unequally diffusible, like the gases, and separations, both mechanical and chemical (decompositions), are

produced by liquid as well as by gaseous diffusion. But it still remains to be found whether the diffusibilities of different salts are in any fixed proportion to each other, as simple numerical relations are known to prevail in the diffusion velocities of the gases, from which their densities are deducible.

It was desirable to make numerous simultaneous observations on the salts compared, in order to secure uniformity of conditions, particularly of temperature. The means of greatly multiplying the experiments were obtained by having the solution phial cast in a mould, so that any number of solution cells could be procured of the same form and dimensions. The phials were of the form represented (fig. 3), holding about 4 ounces, or more nearly 2080 grs. of water to the base of the neck, and the mouths of all were ground down, so as to give the phial a uniform height of 3·8 inches. The mouth or neck was also ground to fit a gauge-stopper of wood, which was 0·5 inch deep and slightly conical, being 1·24 inch in diameter on the upper, and 1·20 inch on the lower surface. These are therefore the dimensions of the diffusion aperture of the new solution cells.

Fig. 3.

A little contrivance to be used in filling the phials to a constant distance of half an inch from the surface of the lip, proved useful. It was a narrow slip of brass plate, having a descending pin of exactly half an inch in length fixed on one side of it (fig. 4). This being laid across the mouth of the phial with the pin downwards in the neck, the solution was poured into the phial till it reached the point of the pin. The brass plate and pin being removed,

Fig. 4.

the neck was then filled up with distilled water, with the aid of the little float as before described. The water-jar, in which the solution phial stood, was filled up with water also as formerly, so as to cover the phial entirely to the depth of 1 inch. This water atmosphere amounted to 8750 grs., or about 20 ounces. A glass plate was placed upon the mouth of the water-jar itself to prevent evaporation. Sometimes 80 or 100 diffusion cells were put in action at the same time. The period of diffusion chosen was now always exactly seven days, unless otherwise mentioned.
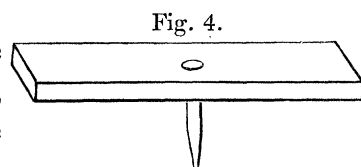
II. DIFFUSION OF SALTS OF POTASH AND AMMONIA.

Solutions were prepared of the various salts, in a pure state, in certain fixed proportions, namely, 2, 4, 6⅔ and 10 parts of salt to 100 parts of water by weight. The density of these solutions was observed by the weighing-bottle, at 60°. The solutions were frequently diffused at two different temperatures; one, the temperature of the atmosphere, which was fortunately remarkably constant during most of the experiments to be recorded at present, and the other, a lower temperature, obtained in a close box of large dimensions, containing masses of ice. The results at the artificial temperature were obviously less accurate than those of the natural temperature, but have still considerable value. Three experiments were generally made upon the diffusion of each solution at the higher, with two experiments at the lower temperature.

(1.) The carbonate and sulphate of potash and sulphate of ammonia were first diffused during a period of seven days, of which the temperatures observed by a thermometer placed near the water-jars were $64°{\cdot}5$, $65°$, $63°{\cdot}5$, $63°$, $63°$, $63°{\cdot}5$, $65°$ and $66°$; mean temperature $64°{\cdot}2$.

TABLE VII.—Diffusion of Carbonate of Potash, Sulphate of Potash and Sulphate of Ammonia.

Parts of anhydrous salt to 100 water.	Density of solution at 60°.	At 64°·2.		At 37°·6.	
		Experiments.	Mean.	Experiments.	Mean.
Carbonate of potash.					
2	1·0178	5·36		3·80	
		5·55	5·45	3·91	3·85
4	1·0347	10·39		6·99	
		10·11	10·25	7·19	7·09
$6\frac{2}{3}$	1·0572	16·50		11·42	
		16·46		11·08	11·25
		17·05	16·67		
10	1·0824	24·42			
		24·94			
		24·70	24·69		
Sulphate of potash.					
2	1·0155	5·62		3·93	
		5·42	5·52	3·98	3·95
4	1·0318	10·49		7·50	
		10·65	10·57	7·31	7·40
$6\frac{2}{3}$	1·0512	17·07		11·62	
		16·89		11·71	11·66
		17·54	17·17		
10	1·0742	23·40			
		23·59			
		23·88	23·62		
Sulphate of ammonia, $NH_4O.SO_5$.					
2	1·0117	5·71		3·73	
		5·45	5·58	3·79	3·76
4	1·0229	10·72		7·54	
		10·30	10·51	7·86	7·70
$6\frac{2}{3}$	1·0369	17·28		10·94	
		16·28		10·98	10·96
		16·80	16·79		
10	1·0529	21·86			
		22·49			
		22·25	22·20		

The diffusion product was obtained by evaporating the water of each jar separately as before, and the result is expressed in grains.

It will be observed at once, on comparing the means of the experiments, that the three salts under consideration are remarkably similar in their diffusion, particularly with the smaller proportions of salt. Thus the mean diffusion of the 2, 4, $6\frac{2}{3}$ and 10 parts of the salts is as follows:—

Diffusion at 64°·2.

	2.	4.	6⅔.	10.
Carbonate of potash	5·45	10·25	16·67	24·69
Sulphate of potash.......................	5·52	10·57	17·17	23·62
Sulphate of ammonia.....................	5·58	10·51	16·79	22·20

Diffusion at 37°·6.

	2.	4.	6⅔.
Carbonate of potash	3·85	7·09	11·25
Sulphate of potash.......................	3·95	7·40	11·66
Sulphate of ammonia.....................	3·76	7·70	10·96

The proportions diffused are sensibly equal, of the different salts, at the higher temperature, with the exception of the largest proportion of salt, 10 per cent., when a certain divergence occurs. This last fact is consistent with our expectations, that the diffusion of salts would prove most highly normal in dilute solutions. Some of the irregularities at the lower temperature are evidently of an accidental kind.

(2.) The neutral chromate and acetate of potash were diffused at a temperature ranging from 63° to 65°, or at a mean temperature of 64°·1, which almost coincides with the higher temperature of the last experiments.

TABLE VIII.—Diffusion of Chromate of Potash and Acetate of Potash, at 64°·1.

Parts of anhydrous salt to 100 water.	Density of solution at 60°.	Experiments.	Mean.
Chromate of potash.			
2	1·0158	5·79	
		5·66	
		5·86	5·77
4	1·0313	11·10	
		11·35	
		11·13	11·19
6⅔	1·0512	17·76	
		17·72	
		17·32	17·60
10	1·0750	24·49	
		24·92	
		24·85	24·75
Acetate of potash.			
2	1·0095	5·93	
		5·75	
		5·88	5·85
4	1·0184	10·55	
		10·56	
		10·98	10·70
6⅔	1·0306	16·53	
		16·06	
		16·84	16·48
10	1·0447	24·27	
		24·82	
		25·46	24·85

We have the same close correspondence in the diffusion products of these two salts as in the preceding group, and here the correspondence extends to the 10 per cent. solution.

Diffusion at 64°·1.

	2.	4.	6⅔.	10.
Chromate of potash	5·77	11·19	17·60	24·75
Acetate of potash	5·85	10·70	16·48	24·85

The 10 per cent. solution of these two salts also agrees with the same solution of carbonate of potash, which was 24·69 grs. Nor do the lower proportions diverge greatly from the preceding group of salts.

(3). Another pair of salts were simultaneously diffused, but with an accidental difference of 0°·4 of temperature.

TABLE IX.—Diffusion of Bicarbonate of Potash, $KO . CO_2 + HO . CO_2$, at 64°·1, and Bichromate of Potash, $KO . 2CrO_3$, at 64°·5.

Parts of anhydrous salt to 100 water.	Density of solution at 60°.	At 64°·1 and 64°·5.	
		Experiments.	Mean.
Bicarbonate of potash. 2	1·0129	5·74 5·77 5·91	
			5·81
4	1·0252	10·75 11·16 11·13	
			11·01
Bichromate of potash. 2	1·0139	5·64 5·73 5·59	
			5·65
4	1·0273	11·55 11·54 11·39	
			11·49

Here again the two salts approach closely in diffusion, and also correspond well with the two preceding series.

Mean Diffusion at 64°·1 and 64°·5.

	2.	4.
Bicarbonate of potash	5·81	11·01
Bichromate of potash	5·65	11·49

It is singular to find that salts differing so much in constitution and atomic weight as the chromate and bichromate of potash, may be confounded in diffusibility. The diffusion products of these two salts are, for the 2 per cent. solutions, 5·77 and 5·65

grs., and for the 4 per cent. solution, 11·19 and 11·49 grs.   The bicarbonate of potash also exhibits a considerable analogy to the carbonate, but resembles still more closely the acetate.   It is thus obvious that equality, or similarity, of diffusion is not confined to the isomorphous groups of salts.

(4.) The nitrates of potash and ammonia have already appeared to be equidiffusive at two different temperatures.   They were diffused again in the same proportions as the last salts, at a temperature varying from 63° to 67°·5.

TABLE X.—Diffusion of Nitrate of Potash and Nitrate of Ammonia at 65°·9.

Parts of anhydrous salt to 100 water.	Density of solution at 60°.	Experiments.	Mean.
Nitrate of potash.			
2	1·0123	7·34	
		7·58	
		7·49	7·47
4	1·0243	13·66	
		14·24	
		14·02	13·97
6⅔	1·0393	22·11	
		22·94	
		22·05	22·37
10	1·0581	32·06	
		32·90	
		32·50	32·49
Nitrate of ammonia, $NH_4 O, NO_5$.			
2	1·0080	7·85	
		7·71	
		7·64	7·73
4	1·0154	14·20	
		14·79	
		14·45	14·48
6⅔	1·0256	23·66	
		23·35	
		22·22	22·74
10	1·0375	34·94	
		33·49	
		34·23	34·22

The solution of nitrate of ammonia of the water-jars was evaporated carefully at a temperature not exceeding 120° FAHR., to prevent loss of the salt by sublimation or decomposition.

Diffusion at 65°·9.

	2.	4.	6⅔.	10.
Nitrate of potash	7·47	13·97	22·37	32·49
Nitrate of ammonia	7·73	14·48	22·74	34·22

Although these salts correspond closely, it is probable that neither the diffusion of these nor the diffusion of any others is absolutely identical.   The nitrate of ammonia appears to possess a slight superiority in diffusion over the nitrate of potash, which

increases with the large proportions of salt in solution.   They are both considerably more diffusible than the seven preceding salts.

(5.) A second pair of isomorphous salts were compared, the chlorides of potassium and ammonium.

TABLE XI.—Diffusion of Chloride of Potassium and Chloride of Ammonium.

Parts of anhydrous salt to 100 water.	Density of solution at 60°.	At 66°·2.		At 64°·7.	
		Experiments.	Mean.	Experiments.	Mean.
Chloride of potassium.					
2	1·0127	7·83		8·03	
		7·72		7·89	7·96
		7·55	7·70		
4	1·0248	15·22		15·21	
		15·59		14·82	15·01
		15·07	15·29		
6⅔	1·0401	24·88		24·83	
		24·64		24·62	24·72
		25·09	24·87		
10	1·0592	36·23			
		37·63	36·93		
Chloride of ammonium.					
2	1·0061	7·10		7·10	
		8·52	7·81	7·24	7·17
4	1·0118	14·55		13·91	
		14·64	14·60	14·91	14·41
6⅔	1·0190	24·30	24·30	24·12	
				24·13	24·12
10	1·0272	36·53	36·53		

These two salts agree well in diffusibility, and are also evidently related to the preceding nitrates.   The quantity of chloride of ammonium diffused was determined by evaporation, which is troublesome and may lead to small errors, from the volatility and efflorescent tendency of this salt.   It would be easier and more accurate to determine this and other chlorides by the use of a normal solution of nitrate of silver, and so avoid evaporation.

Diffusion at 66°·2.

	2.	4.	6⅔.	10.
Chloride of potassium	7·70	15·29	24·87	36·93
Chloride of ammonium	7·81	14·60	24·30	36·53

The quantities diffused of these two chlorides are more closely in proportion to the strength of the original solution, than with any of the preceding salts of potash. Thus the quantities diffused from the 2 and 10 per cent. solutions of chloride of potassium are 7·70 and 36·93 grs., which are as 2 to 9·6, which is nearly as 2 to 10. Chloride of sodium was observed before to be nearly uniform in this respect; but other salts appear to lose considerably in diffusibility with the higher proportions of

salt. It is possibly a consequence of the crystallizing attraction, to which reference was lately made, coming into action in strong solutions and resisting diffusion.

(6.) The diffusion of chlorate of potash was observed at a temperature ranging from 63° to 65°, of which the mean was 64°·1.

TABLE XII.—Diffusion of Chlorate of Potash.

Parts of salt to 100 water.	Density of solution at 60°.	At 64°·1.	
		Experiments.	Mean.
2	1·0129	6·97 7·54 7·16	7·22
4	1·0246	13·03 13·64 13·27	13·31
6·5 (saturated solution).	1·0395	21·30 20·29 20·76	20·78

The solutions of chlorate of potash must be evaporated and the residuary salt dried at a temperature not exceeding 212°, otherwise a very sensible quantity of chloride of potassium may be formed. The chlorate appears to be sensibly inferior in diffusibility to the nitrate of potash. From the 4 per cent. solution of the chlorate we have a diffusion product of 13·27 grs., and from the corresponding solution of the nitrate 13·97 grs.; but the latter was obtained at a temperature 1°·8 higher than the former. It remains a question whether chlorate of potash does not really belong to the nitre group of salts, but has its diffusion interfered with by some secondary agency, such as its sparing solubility and consequent nearer approach to the saturating proportion.

It is certainly true that the uniformity of diffusion generally increases with the dilution of the solutions. This appears on comparing the diffusion of the 4 per cent. solution of what may be called the sulphate of potash group, with the diffusions of the 2 per cent. solutions of the same salts.

Diffusion of Salts of the Sulphate of Potash Class.

	4.	2.
Carbonate of potash	10·27	5·45
Sulphate of potash	10·57	5·52
Sulphate of ammonia.........	10·51	5·58
Acetate of potash	10·70	5·85
Bicarbonate of potash	11·01	5·81
Chromate of potash	11·19	5·77
Bichromate of potash	11·49	5·65

Thus while the 4 per cent. solutions range from 10·27 to 11·49 grs., or from 100 to 111·8, the 2 per cent. solutions range from 5·45 grs. to 5·85 grs., or from 100 to 107·3.

As it appeared to be in dilute solutions that the greatest uniformity of diffusion is to be expected, a series of experiments was instituted upon the preceding salts, with

the addition of acetate of potash, which appeared to belong to the same class, the solution employed being that of 1 salt to 100 water. The experiments were made in a vault, of which the temperature was nearly uniform, falling in a gradual manner from 59° to 58°, with a mean of 58°·5 during the period of seven days which the diffusion lasted. Eight phials of each salt were diffused, and the liquids of four water-jars evaporated together.

Carbonate of potash gave 10·42 and 10·59 grs. of salt diffused: mean 10·51 grs., or 2·63 grs. for one cell.

Sulphate of potash gave 10·72 and 10·78 grs. of salt diffused: mean 10·75 grs., or 2·69 grs. for one cell.

Acetate of potash, its diffusion product being treated with an excess of hydrochloric acid, gave 8·30 and 8·04 grs. of chloride of potassium, equivalent to 10·91 and 10·57 grs. of acetate of potash; mean 10·74 grs. of acetate of potash, or 2·68 grs. for one cell. The diffusion of these three salts is therefore remarkably similar:—

Diffusion of 1 *per cent. solutions at* 58°·5.

Carbonate of potash . . . . 2·63 grs.
Sulphate of potash . . . . 2·69 grs.
Acetate of potash . . . . . 2·68 grs.

The 1 per cent. solution of neutral or yellow chromate of potash in good crystals gave 11·28 and 11·35 grs.; mean 11·31 grs., or 2·83 grs. for each cell. It was remarked of the diffused chromate in this experiment, that it contained a sensible quantity of green oxide of chromium. The diffusion of a salt appears indeed to try its tendencies to decomposition very severely.

The bicarbonate of potash gave 8·83 and 8·35 grs. of chloride of potassium, the diffusion product being neutralized with hydrochloric acid; equivalent to 11·25 and 11·21 grs. of bicarbonate of potash; mean 11·23 grs., or 2·81 grs. for one cell.

The bichromate of potash gave 11·54 and 11·49 grs. of salt diffused; mean 11·51 grs., or 2·88 grs. for one cell. These last three salts give all a larger diffusion product than the preceding three, while they agree well together. It is doubtful whether this excess in their diffusion is occasioned by a partial decomposition in the act of diffusion, which might be of such a kind as to increase the real or apparent diffusion in every one of them, or whether it is a peculiar character of this little group, to which the ferricyanide of potassium, it will be afterwards seen, falls to be added, while the ferrocyanide appears to belong to the other group:—

Diffusion of 1 *per cent. solutions at* 58°·5.

Chromate of potash . . . . 2·83 grs.
Bicarbonate of potash . . . 2·81 grs.
Bichromate of potash . . . . 2·88 grs.

The divergence from each other of two salts so closely isomorphous as sulphate and

chromate of potash, in the proportion of 100 to 105·2, is certainly remarkable, unless due to a slight decomposition of the latter.

(7.) *Ferrocyanide and Ferricyanide of Potassium.*

Of these two salts the 1 per cent. solution only was diffused. The time of diffusion was seven days, as usual; the mean temperature 54°·5. In evaporating the liquid of the water-jars, both salts were partially decomposed, so that it became necessary to estimate the diffusion product by a determination of the potash. Eight cells were employed for one salt and six for the other, and the liquids of the water-jars evaporated two together.

The diffusion product of ferrocyanide of potassium (anhydrous) was 5·02, 5·22, 5·02 and 5·20 grs.; mean 5·12 grs., or for one cell 2·56 grs.

The diffusion product of ferricyanide of potassium was 5·54, 5·64 and 5·36 grs.; mean 5·51 grs., or for one cell 2·75 grs.

Three cells of a similar solution of sulphate of potash which were diffused for seven days at a mean temperature 1° lower, or of 53°·5, gave 2·56, 2·53 and 2·62 grs.; mean for one cell 2·57 grs., a number which almost coincides with that of the ferrocyanide of potassium (2·56 grs.). The ferricyanide of potassium, on the other hand, is sensibly more diffusive, as 107·6 to 100, and appears to rank with the bicarbonate and bichromate of potash. The ferricyanide of potassium, again, is a salt which probably undergoes a slight decomposition in diffusion like those salts mentioned:—

Diffusion of 1 *per cent. solutions.*

Sulphate of potash . . . . . 2·57 grs. at 53°·5.
Ferrocyanide of potassium . . 2·56 grs. at 54°·5.
Ferricyanide of potassium . . 2·75 grs. at 54°·5.

The salts of the nitre class may also be compared in the same manner, and I shall now add a third series of results obtained from the diffusion of 1 per cent. solutions of the same salts. The temperature of diffusion of this new series was 64°·5. Six phials of each salt were diffused, and they were evaporated afterwards two and two. This double diffusion product, however, is divided by 2 in the table.

Diffusion of Salts of the Nitre Class.

	4.	2.	1.
Nitrate of potash	13·97	7·47	3·72
Nitrate of ammonia	14·48	7·73	3·75
Chloride of potassium	15·01	7·70	3·88
Chloride of ammonium	14·41	7·81	3·89
Chlorate of potash............	13·31	7·22	3·66
Mean	14·23	7·58	3·78

It is interesting to observe how the chlorate of potash rises in the lower proportions and approaches to the normal rate of its class. The diffusion products of all the salts are obviously more uniform for the two than for the 4 per cent. solutions, and again more uniform for the 1 than for the 2 per cent. solutions. The extremes in the 1 per cent. solutions are 3·66 grs. chlorate of potash, and 3·89 grs. chloride of ammonium, which are as 1 to 1·0628. We have here an approach to equality in diffusion, which appears to be as close as the experimental determinations are of the specific heat of different bodies belonging to one class. The numbers for the specific heat of equivalents of the metallic elements are known to vary as 38 to 42.

The salts of potash thus appear to fall into two groups of very similar if not equal diffusibility. What is the relation between these groups?

The diffusion of 4 per cent. solutions of carbonate and nitrate of potash was repeated at a temperature rising gradually from 63° to 65° during the seven days of the experiment, with a mean of 64°·1. The diffusion products of the carbonate were 10·31, 10·05 and 10·44 grs. in three cells; mean 10·27 grs. Of the nitrate, 13·98, 13·86 and 13·60 grs.; mean 13·81 grs. We have thus a diffusion in equal times of—

Carbonate of potash . 10·27   1
Nitrate of potash . . 13·81   1·3447

These experiments are almost identical with the former results, 10·25 carbonate of potash, and 13·97 nitrate of potash.

But the numbers thus obtained cannot be fairly compared, owing to the diminishing progression in which the diffusion of a salt takes place. Thus when the diffusion of nitrate of potash was interrupted every two days, as in a former experiment with chloride of sodium, the progress of the diffusion for eight days was found to be as follows in a 4 per cent. solution, with a mean temperature of 66°.

Nitrate of Potash.

Diffused in first two days . . . . 4·54 grs.
Diffused in second two days . . . 4·13 grs.
Diffused in third two days . . . 4·06 grs.
Diffused in fourth two days . . . 3·18 grs.
                                   ‾‾‾‾‾‾
                                   15·91

The absence of uniformity in this progression is no doubt chiefly due to the want of geometrical regularity in the form of the neck and shoulder of the solution phial. A plain cylinder, as the solution cell, might give a more uniform progression, but would increase greatly the difficulties of manipulation.

The diffusion of carbonate of potash will no doubt follow a diminishing progression also; but there is this difference, that the latter salt will not advance so far in its progression, owing to its smaller diffusibility, in the seven days of the experiment, as the more diffusible nitrate does. The diffusion of the carbonate will thus be given

in excess, and as it is the smaller diffusion, the difference of the diffusion of the two salts will not be fully brought out.

The only way in which the comparison of the two salts can be made with perfect fairness, is to allow the diffusion of the slower salt to proceed for a longer time, till in fact the quantity diffused is the same for this as for the other salt, and the same point in the progression has therefore been obtained in both; and to note the time required. The problem takes the form of determining the times of equal diffusion of the two salts. This procedure is the more necessary from the inapplicability of calculation to the diffusion progression.

Further, allowing the Times of Equal Diffusion to be found, it is not to be expected that they will present a simple relation. Recurring to the analogy of gaseous diffusion, the times in which equal volumes or equal weights of two gases diffuse are as the square roots of the densities of the gases. The times, for instance, in which equal quantities of oxygen and hydrogen escape out of a vessel into the air, in similar circumstances, are as 4 to 1; the densities of these two gases as 16 to 1. Or, the times of equal diffusion of oxygen and protocarburetted hydrogen are as 1·4142 to 1, that is as the square root of 2 to the square root of 1; the densities of these gases being 16 and 8, which are as 2 to 1. The densities are the squares of the equal-diffusion times. It is not therefore the times themselves of equal diffusion of two salts, but the squares of those times which are likely to exhibit a simple relation.

(1.) While the 4 per cent. solution of nitrate of potash was diffused as usual for seven days, the corresponding solution of carbonate of potash was now allowed to diffuse for 9·90 days; times which are as 1 to 1·4142, or as 1 to the square root of 2.

The results were as follows: diffused of—

Nitrate of potash at 64°·1, in seven days, 13·81 grs.   .   .   100
Carbonate of potash at 64°·3, in 9·9 days, 13·92 grs.   .   .   100·8

The three experiments on the nitrate of potash, of which 13·81 grs. is the mean, were 13·98, 13·86 and 13·60 grs., as already detailed. The three experiments on the carbonate were 14·00, 13·97 and 13·78 grs. The difference in the means of the two salts is only 0·11 gr. The results appear to be as near to equality as could be reasonably expected from the method of experimenting. Seven and 9·90 may therefore be considered as the times of equal diffusion indicated for nitrate and carbonate of potash. The times of equal diffusion, or the diffusibilities of nitrate and carbonate of potash, would appear therefore to be in the proportion of the square root of 1 to the square root of 2.

The explanation of such a relation suggested by gaseous diffusion has been anticipated. It is that the two salts have different densities in solution, that of nitrate of potash being 1, and that of carbonate of potash 2. We are thus led to ascribe, what may be called Solution Densities, to the salts. The two salts in question are related exactly like protocarburetted hydrogen gas, of density 1, to oxygen gas of density 2. The parallel would be completed by supposing that the single volume of oxygen to

be diffused was previously mixed with 100 volumes of air (or any other diluting gas), while the 2 volumes of protocarburetted hydrogen were also diluted with 100 volumes of air; the diluting air here representing the water in which the salts to be diffused are dissolved in the solution cell. The time in which a certain quantity of protocarburetted hydrogen would come out from a vessel containing 1 per cent. of that gas being 1 (the square root of density 1), the time in which an equal quantity of oxygen would diffuse out from a similar vessel containing 1 per cent. also would be 1·4142 (the square root of density 2).

(2.) A solution of 4 parts of sulphate of potash in 100 water was diffused simultaneously with the last solution of carbonate of potash, and therefore in similar circumstances. The diffusion products of three experiments were 14·46, 14·21 and 14·53 grs.; mean 14·40 grs. This is in the proportion of 104·27 sulphate of potash to 100 nitrate of potash; so that the approximation to equality of diffusion with nitrate of potash, in the selected times, is not so close for the sulphate as for the carbonate of potash.

(3.) The diffusion was repeated of 2 per cent. solutions of the nitrate and carbonate of potash at a lower temperature by about 10°. The temperature of the solutions was rather unsteady; ranging from 56° to 52°·25 for the first period of seven days, from 56° to 50°·5 for the period of 9·90 days, and from 55° to 50°·5 for a second period of seven days; the external atmospheric temperature having fallen during the same period more than 20 degrees. Six phials of each solution were diffused and evaporated two together; so that the results are all double quantities.

At a mean temperature of 54°·3, the nitrate of potash gave in seven days 12·60 and 12·13 grs.; mean 12·36 grs.

Again, at a mean temperature of 52°·4, the nitrate of potash gave in seven days 11·85, 12·40 and 11·95 grs.; mean 12·06 grs.

The carbonate of potash gave in 9·90 days, with a mean temperature of 53°·4, 12·69, 12·40 and 12·12 grs.; mean 12·40 grs.

The general results are—

        Nitrate of potash, in seven days, at 54°·3 .   12·36 grs.
        Carbonate of potash, in 9·9 days, at 53°·4 .   12·40 grs.
        Nitrate of potash, in seven days, at 52°·4 .   12·06 grs.

As the first nitrate is 0°·9 above the carbonate and the second nitrate 1° below it, we may take the mean of the two nitrates as corresponding to the temperature of the carbonate. We thus finally obtain, diffused at 53°·4, of—

        Nitrate of potash in seven days, 12·22 grs. . . 100
        Carbonate of potash in 9·9 days, 12·40 grs. . . 101·47

The difference in the amount of the diffusion of the two salts in these times is only 0·18 gr., or 1½ per cent.

These last experiments may be held therefore as tending to the same conclusion as

the former series, although the circumstances were more than usually unfavourable to their success. To find whether the same relation existed between the salts through a considerable range of temperature, an opportunity was taken during cold weather to repeat the experiments at a low temperature.

(4.) Solutions of 1 salt in 100 water were diffused from eight solution cells, for each salt. The times were increased, but the same ratio of 1 to 1·4142 was preserved between them. The liquids of the cells were found to retain a temperature ranging slowly between 41° and 38°·8 during the whole period of the observations. Sulphate of potash was substituted for the carbonate, as of these two equi-diffusive salts the former had been found to be least in accordance with nitrate of potash, in the 4 per cent. solutions, and appeared therefore to afford the severest test of the relation.

For nitrate of potash, at a mean temperature of 39°·7, during nine days, the diffusion product of two cells together was 6·97, 6·93, 6·77 and 6·64 grs.; mean 6·83 grs. for two cells.

For sulphate of potash, at the same mean temperature of 39°·7, during 12·728 days (twelve days, seventeen hours, twenty-eight minutes), the diffusion product of two cells together was 7·05, 6·93, 7·28 and 6·90 grs.; mean 7·04 grs. for two cells.

The general results are—

Nitrate of potash in nine days at 39°·7 . . 6·83 grs. . . 100

Sulphate of potash in 12·728 days at 39°·7 7·04 grs. . . 103·07

(5.) Solutions of 2 salt in 100 water were diffused simultaneously with the preceding experiments, and in precisely the same conditions of time and temperature.

The diffusion product of nitrate of potash during nine days, at a mean temperature of 39°·7, was 7·03, 6·63, 6·83 and 6·83 grs. for one cell; mean 6·83 grs. for one cell, or the same number as for two cells with the 1 per cent. solution.

The diffusion product of sulphate of potash during 12·728 days was 6·84, and 6·80; mean 6·82 grs. for one cell. These experiments almost coincide with the number for nitrate of potash.

Nitrate of potash, 6·83 grs. 100

Sulphate of potash, 6·82 grs. . . . . 99·85

(6.) The existence of the relation in question was also severely tested in another manner. Preserving the ratio in the times of diffusion for the two salts, the actual times were varied in duration, in three series of experiments, as 1, 2 and 3. The experiments were made in the vault, with a uniformity of temperature favourable to accuracy of observation. Eight cells of the 1 per cent. solution of each salt were always diffused at the same time.

(a.) Nitrate of potash diffused for 3·5 days, at 47°·2, gave for two cells, 3·55, 3·63, 3·33 and 3·51 grs.; mean for two cells, 3·50 grs.

Sulphate of potash diffused for 4·95 days, at 47°·3, gave for two cells, 3·54, 3·31,

3·51 and 3·63 grs.; mean for two cells, 3·50 grs., or exactly the same as for nitrate of potash above.

(*b.*) Nitrate of potash diffused for seven days, at 48°·6, gave 6·1, 6·2, 5·9 and 5·92 grs.; mean for two cells, 6·04 grs.

Sulphate of potash diffused for 9·9 days, at 49°·1, gave 6·13, 5·92, 6·18 and 6·59 grs.; mean 6·20 grs., or, excluding the last experiment, 6·08 grs.

Chromate of potash diffused also for 9·9 days, at 49°·1, gave 6·19, 6·18, 6·40 and 6·38 grs.; mean for two cells, 6·29 grs. The diffused chromate presented no appearance of decomposition on this occasion.

(*c.*) Nitrate of potash diffused for 10·5 days, at 48°, gave 8·36, 8·95, 8·82 and 8·84 grs.; mean for two cells, 8·74 grs.

Sulphate of potash diffused for 14·85 days, at 48°·6, gave 8·99, 8·94, 8·66 and 8·56 grs.; mean for two cells, 8·79 grs.

The mean results for the three different sets of periods of diffusion are as follows:—

3·5 and 4·95 days {
Nitrate of potash, at 47°·2, 3·50 grs. . . . 100
Sulphate of potash, at 47°·3, 3·50 grs. . . . 100

7 and 9·9 days {
Nitrate of potash, at 48°·6, 6·04 grs. . . . 100
Sulphate of potash, at 49°·1, 6·20 grs. . . . 102·65
Chromate of potash, at 49°·1, 6·29 grs. . . 104·14

10·5 and 14·85 days {
Nitrate of potash, at 48°, 8·74 grs. 100
Sulphate of potash, at 48°·6, 8·79 grs. . . . 100·57

The concurring evidence of these three series of experiments appears to be quite decisive in favour of the assumed relation of 1 to 1·4142, between the times of equal diffusion for the nitrate and sulphate of potash, and consequently of the times for the two classes of potash salts, of which the salts named are types. The same experiments are also valuable as proving the similarity of the progression of diffusion, in two salts of unequal diffusibility. I shall return again to the relation between nitrates and sulphates, under the salts of soda.

(8.) *Hydrate of Potash.*

(1.) Eight cells of the 1 per cent. solution of pure fused hydrate of potash were diffused for seven days in the vault, with a temperature ranging only from 59° to 58°, of which the mean was 58°·6. The product of four cells evaporated together was 17·57 grs. of hydrate of potash, and of the other four cells 17·19 grs.; mean 17·38 grs., or 4·345 grs. for one cell. The hydrate of potash was estimated from the chloride of potassium which it gave when saturated with hydrochloric acid. The diffusion product of sulphate of potash for seven days, at 58°·5, or almost the same temperature, was 10·75 grs. for the four cells, as already stated, and consequently 2·64 grs. for one cell. It thus appears that the hydrate of potash is greatly more diffusive than the sulphate of potash in the same period of seven days, namely, as 4·345 to 2·64.

Such a result indeed is not inconsistent with the times of equal diffusion of these two substances, differing as much as 1 to 2.

(2.) Of pure fused hydrate of potash, a 1 per cent. solution was diffused from four cells for 4·95 days at a mean temperature of 53°·7, against a 1 per cent. solution of nitrate of potash in six cells, for seven days, at a mean temperature 0°·1 lower, or of 53°·6. The hydrate of potash which diffused, is calculated as before from the chloride of potassium which it gave, when neutralized by hydrochloric acid. Hydrate of potash diffused from two cells 5·97 and 6·28 grs.; mean 6·12 grs., or 3·06 grs. for a single cell.

Nitrate of potash diffused from two cells 6·22, 6·54 and 5·93 grs; mean 6·23 grs., or 3·11 grs. for a single cell. The diffusion of nitrate of potash being 100, that of the hydrate of potash is 98·2, numbers which are sufficiently in accordance. But the times were as 1 to 1·4142, and their squares as 1 to 2. So far then as this series of experiments on hydrate of potash entitles us to conclude, we appear to have for the salts of potash a close approximation to the following simple series of squares of equal diffusion times :—

Squares of Times of Equal Diffusion, or Solution Densities.

Hydrate of potash 1
Nitrate of potash 2
Sulphate of potash 4

(3.) The hydrate of potash was also diffused at the lower temperature, 39°·7, in company with the nitrate and sulphate of potash for a period of 6·364 days (six days, eight hours, forty-four minutes).

The 1 per cent. solution of hydrate of potash gave in eight cells, evaporated two together, 6·93, 6·93, 6·93 and 6·89 grs.; mean 6·92 grs.

The 2 per cent. solution of hydrate of potash gave in three single cells, 6·77, 6·49 and 7·10 grs.; mean 6·79 grs.

The diffusion of nitrate of potash in nine days at the same temperature, as already detailed, was sensibly the same, or 6·83 grs. for both the 1 and 2 per cent. solutions. The times for the two salts were as 1 to 1·4142.

The diffusion of hydrate of potash, at 39°·7, may therefore be stated with reference to that of nitrate of potash, for the selected times, as follows :—

Nitrate of potash, 1 and 2 per cent. solutions. 100
Hydrate of potash, 1 per cent. solution . . . . 101·3
Hydrate of potash, 2 per cent. solution . . . . . . 99·4

These experiments at the low temperature concur, therefore, with those made at the higher temperature, in proving that the times of equal diffusion of the two substances have been properly chosen.

III. DIFFUSION OF SALTS OF SODA.

(1.) The only salts of soda which I have yet had an opportunity of diffusing in a sufficient variety of circumstances are the carbonate and sulphate. These salts appear to be equi-diffusive, but to diverge notwithstanding more widely in the solutions of the higher proportions of salt than the corresponding potash salts. It is a question whether this increased divergence is not due to the less solubility of the soda salts, and the nearer approach consequently to their points of saturation in the stronger solutions.

TABLE XIII.—Diffusion of Carbonate and Sulphate of Soda.

Parts of anhydrous salt to 100 water.	Density of solution at 60°.	At 64°.		At 37°·7.	
		Experiments.	Mean.	Experiments.	Mean.
Carbonate of soda.					
2	1·0202	4·15		2·78	
		4·08		2·62	
		4·21	4·14	2·73	2·71
4	1·0405	7·96		5·31	
		7·70		4·94	
		7·68	7·78	5·35	5·20
6⅔	1·0653	12·16		8·50	
		12·06		8·45	
		12·45	12·22	8·05	8·33
10	1·0957	17·13			
		16·53			
		17·00	16·88		
Sulphate of soda.					
2	1·0179	4·35		2·96	
		4·32		3·03	
		4·25	4·31	3·09	3·03
4	1·0352	8·14		5·63	
		8·10		5·64	
		8·28	8·17	5·42	5·56
6⅔	1·0578	13·26		8·77	
		13·63		8·84	8·80
		13·61	13·50		
10	1·0847	18·71			
		19·73			
		18·91	19·14		

The range of the thermometer during the continuance of the experiments at the higher temperature was from 64°·5 up to 65° and falling again to 63°; the mean of all the days being 64°. The temperature of the other series, or of the ice-box, was 42° the first day, 38° the second, and 37° steadily for the remainder of the period; the mean being 37°·7.

The mean results at 64° are as follows :—

	2.	4.	6⅔.	10.
Carbonate of soda	4·14	7·78	12·22	16·88
Sulphate of soda	4·31	8·17	13·50	19·14

Another series of experiments was made upon a 1 per cent. solution of the same salts at a mean temperature of 64°·9. Six phials of each solution were diffused, and the water of two jars afterwards evaporated together, so that the quantities stated are double.

The diffusion product in three experiments with the sulphate of soda was 4·77, 4·75 and 4·80 grs.; mean 4·77 grs. The diffusion product in three experiments with the carbonate of soda was 4·61, 4·68 and 4·67 grs.; mean 4·65 grs. The difference between the carbonate and sulphate is 0·12 gr.; it is less for the present proportion of 1 per cent. of salt, than for 2 per cent., so that the diffusion of the salts may be converging to a perfect equality in very weak solutions. One-half of the preceding quantities, or the mean results for a single diffusion cell, are—

Diffusion of 1 per cent. solutions at 64°·9.

Carbonate of soda, 2·32 grs. 100
Sulphate of soda, 2·38 grs. . . . . 102·58

(2.) The diffusion of the carbonate of soda was further compared with the nitrate of the same base, to find whether their times of equal diffusion are related like those of the corresponding potash salts. The mean temperature of the first seven days, which was the period of diffusion for the nitrate of soda, was 66°·9; of the last three days, 65°·2; and of the whole period of 9·9 days occupied by the carbonate of soda, 66°·4. The 4 per cent. solutions were employed.

The nitrate of soda gave a diffusion product, in three experiments, of 11·48, 11·58 and 12·13 grs.; mean 11·73 grs.

The carbonate of soda, in three experiments, gave 11·66, 11·53 and 11·52 grs.; mean 11·57 grs. A slight addition should be made to the latter quantity to raise the diffusion product from 66°·4 to 66°·9. It will appear from a subsequent experiment that the diffusion of the carbonate of soda increases 0·096 gr. for a rise of one degree of temperature; which will give 0·05 gr. for the half degree in question. Bringing the diffusion of the two salts to the same temperature of 66°·9, we have therefore diffused, of—

Nitrate of soda, in seven days, 11·73 grs. 100
Carbonate of soda, in 9·9 days, 11·62 grs. . . . . . 99·06

The difference in the quantity diffused of the two salts is only 0·11 gr., or 1 per cent., which is quite within the unavoidable errors of observation.

(3.) The diffusion of a 2 per cent. solution of the same salts was repeated at the same inferior temperature of 54°·3 as with the salts of potash, and under the same difficulties from fluctuation of atmospheric temperature. Two water-jars were evaporated together, so that the results are double.

Nitrate of soda, diffused for seven days at a mean temperature of 54°·3, gave 10·15, 10·24 and 9·92 grs. in three experiments; mean 10·10 grs.

Carbonate of soda, diffused for 9·9 days at a mean temperature of 53°·4, gave 9·93, 9·54 and 10·10 grs. in three experiments; mean 9·86 grs. But the latter amount is to be increased by 0·09 gr. to bring it to the diffusion of 54°·3. We have then for the diffusion product of the two salts at the same temperature of 54°·3—

<div align="center">

Nitrate of soda, in 7 days, 10·10 grs. 100

Carbonate of soda, in 9·9 days, 9·95 grs. . . . 98·51

</div>

The difference is again small, namely, 0·15 gr., or $1\frac{1}{2}$ per cent., and within the limits of unavoidable error.

It appears therefore that the times of equal diffusion of the nitrate and carbonate of soda are related like those of the nitrate and carbonate of potash, or as the square root of 1 and 2, that is, as 1 to 1·4142.

Relation of Salts of Potash to Salts of Soda.

It appeared probable, from many of the experiments already recorded, that if any relation, in the times of equal diffusibility, existed between the corresponding salts of potash and soda, it was that of the square root of 2 to the square root of 3. They were accordingly diffused for times having this ratio; namely, the nitrate of potash for seven days, the nitrate of soda for 8·57325 days; the sulphate and carbonate of potash for 9·9 days, and the sulphate and carbonate of soda for 12·125 days. If these times are rightly chosen, the eventual diffusion products of all the experiments should be equal. The 1 per cent. solution was selected, and the number of experiments simultaneously made on each salt was eight or six. The liquids of two water-jars were evaporated together, so that each of the results in the table below represents the diffusion of two cells. These experiments also afford another opportunity of testing the assumed relation between the nitrates and sulphates of the same base.

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TABLE XIV.—Solution: 1 Salt to 100 Water, at 55°·4—56°·1.

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	Tempe- rature.	Time in days.	Square of times. Sol. density.	Diffusion product of two cells in grs.				
				Exp. I.	Exp. II.	Exp. III.	Exp. IV.	Mean.
Nitrate of potash	56·1	7	2	6·67	6·87	6·90	6·57	6·75
Nitrate of soda	55·7	8·57	3	6·59	6·80	6·94	6·57	6·78
Sulphate of potash	55·4	9·90	4	6·73	6·77	6·96	6·68	6·78
Sulphate of soda	55·4	12·125	6	6·43	6·94	6·80	6·68	6·72
Carbonate of potash	55·4	9·90	4	6·54	6·64	6·40	6·67	6·56
Carbonate of soda	55·4	12·125	6	6·40	6·63	6·60	6·67	6·54

The range of temperature during the period of these experiments rather exceeded 3 degrees, so that they cannot be considered as fortunate in that respect; but still the similarity between the different sets of experiments, and the near equality of their means, is very remarkable. The two nitrates and the two sulphates may be said to coincide, the extreme difference of the means of the four salts not being quite so much as 1 per cent. The two carbonates fall about 3·4 per cent. below the sul-

phates and nitrates, but agree perfectly with each other, showing a uniformity in their irregularity. This deviation of the carbonates would appear essential, as it has been observed every time they have been compared with the sulphates.

The double relation between salts of potash and salts of soda, and between the nitrate and sulphate class of each of these bases, will, I believe, be allowed to acquire considerable additional support from this new series of observations.

IV. DIFFUSION OF SULPHATE OF MAGNESIA.

In a set of preliminary experiments upon sulphate of magnesia in comparison with sulphate of potash, the 4 per cent. solutions of both salts were diffused for seven days at a mean temperature of $57°·9$, with very little fluctuation, the extreme range being from $58°·5$ to $57°·75$. The sulphate of magnesia is taken anhydrous in all the following experiments. The diffusion of sulphate of potash in three cells was 9·16, 9·22 and 9·57 grs.; mean 9·32 grs.

The diffusion of sulphate of magnesia in three cells was 5·21, 4·98 and 5·34 grs.; mean 5·18 grs. The diffusion, in equal times, appears here to be as 100 sulphate of potash to 55·58 sulphate of magnesia. We know, however, when unequally diffusible salts are diffused for equal times, that the diffusion of the slower is exaggerated. Consequently the diffusion of sulphate of magnesia is likely to be represented in excess in these experiments.

In a second preliminary series of experiments the same 4 per cent. solutions were diffused, the sulphate of potash for eight days and the sulphate of magnesia for nineteen days, with the view of discovering their times of equal diffusibility.

During the first period of eight days the temperature fluctuated considerably, beginning at $54°$, falling gradually in four days to $50°·5$, and rising again in four days to $53°$; the average of the whole period was $52°·2$. The diffusion of sulphate of potash from three cells was 9·36, 9·25 and 10·52 grs.; mean 9·71 grs.

During the second period of nineteen days, which included the first period, the mean temperature was $54°·6$. The diffusion of sulphate of magnesia from three cells was 11·81, 11·61 and 10·90 grs.; mean 11·44 grs. The variation in the amounts diffused of both salts is greater than usual, owing no doubt to the changes of temperature, which were imperfectly controlled.

Dividing the quantity of salt diffused by the number of days, we have of sulphate of potash 1·214 gr. diffused per day, and of sulphate of magnesia 0·602 gr. per day; or the latter salt exhibits sensibly half the diffusibility of the former in equal times. This suggested the trial of times for these two salts in the proportion of 1 to 2, with the view of obtaining equal diffusions.

(1.) A one per cent. solution of sulphate of magnesia (anhydrous) was diffused for the long period of 19·8 days, at a mean temperature of $54°·7$, in eight cells. The diffusion products of four pairs of cells were 7·07, 6·71, 7·07 and 7·35 grs.; mean 7·05 grs., or for one cell, 3·53 grs.

A similar solution of sulphate of potash diffused for 9·9 days, or half the preceding period, at a mean temperature of 55°·4, or 0°·7 higher, gave a mean product, for two cells, of 6·79 grs., as before stated, or for one cell, of 3·40 grs. The diffusion of sulphate of potash being 100, that of sulphate of magnesia is therefore 103·7, a fair approximation to equality.

(2.) In a second series of experiments upon 1 per cent. solutions of the same two salts, diffused in the vault for fourteen and seven days respectively, with a mean temperature of 53°·8 for the sulphate of magnesia, and 54°·3 for the sulphate of potash, the temperature was remarkably uniform, gradually falling from 55°·2 to 53° during the longer period, but without any injurious oscillation.

From eight cells, evaporated two together, the sulphate of magnesia obtained was 6·12, 6·12, 6·04 and 6·03 grs.; mean 6·08 grs., or 3·04 grs. for one cell.

The sulphate of potash gave from eight cells, in experiments already detailed, a mean result of 5·84 grs. of salt for two cells, or 2·92 grs. for one cell. The diffusion is in the proportion of 100 sulphate of potash to 104·11 sulphate of magnesia, the times being as 1 to 2 for the two salts respectively.

From these two series of experiments, it appears that, at 54°, sulphate of magnesia has nearly, if not exactly, half the diffusibility of sulphate of potash, and consequently one-fourth of that of hydrate of potash. Or, the times of equal diffusion for these three salts appear to be 1, 2 and 4. The squares of these times and the solution densities are 1, 4 and 16. Hydrate of potash may possibly therefore have the same relation to sulphate of magnesia in solution density and diffusibility that hydrogen gas has to oxygen gas.

(3.) A two per cent. solution of sulphate of magnesia, diffused for fourteen days, gave at 53°·9, for two pairs of cells, 9·57 and 10·00 grs. of salt, of which the mean is 9·79 grs., or 4·85 grs. for one cell.

A similar solution of sulphate of potash diffused for seven days gave a mean result of 4·97 grs. of salt for one cell, at 54°·2, as already stated. The result is a diffusion of 100 sulphate of potash to 97·59 sulphate of magnesia.

(4.) A four per cent. solution of sulphate of magnesia, diffused for fourteen days, gave at 53°·7, in two pairs of cells, 18·00 and 18·20 grs. of salt; mean 18·10 grs. for two cells, or 9·05 grs. for a single cell.

A similar solution of sulphate of potash, diffused for seven days at 54°·2, gave a mean result of 9·30 grs. of salt for a single cell, as already stated. This is a diffusion of 100 sulphate of potash to 97·4 sulphate of magnesia.

The diffusion of the 2 and 4 per cent. solutions of sulphate of magnesia is so nearly equal to the diffusion of the same proportions of sulphate of potash in half the time, that they may be considered as supplying additional support to the assumed relation between the diffusibilities of these salts.

I may add, that a 4 per cent. solution of anhydrous sulphate of zinc was diffused for fourteen days, simultaneously with the similar solution of sulphate of magnesia,

and of course at the same temperature of 53°·7. Two cells, evaporated two together, gave 17·40 and 17·36 grs. of ignited sulphate of zinc; mean 17·38 grs. The salt remained, after ignition, entirely soluble. This is a diffusion of 8·69 grs. for one cell, while the sulphate of magnesia gave 9·05 grs.; or of 100 sulphate of zinc to 104·14 sulphate of magnesia. This result is interesting, as we here find two salts which are isomorphous, and of which the equi-diffusion is on that account in a high degree probable, differing between themselves so much as 4 per cent.

Another numerous series of experiments was made at a considerably lower temperature, with the view of testing several of the same relations. The temperature in commencing the diffusion was 41°, but fell in the course of three days to 38°·8, and afterwards rose to 39°, from which it never varied afterwards more than a degree during the diffusion of the salts of potash and soda. The mean temperature for their periods did not vary above 0°·1 or 0°·2 from 39°·7, so that it may be supposed the same for all these salts. For the sulphates of magnesia, the mean temperature was 38°·9, or 0°·8 lower. The times chosen are as the square-roots of 2, 3, 6 and 16.

TABLE XV.—Solutions of 1 and 2 Salt to 100 Water, at 39°·7.

	Time in days.	Square of times. Sol. density.	Diffusion product of two cells in 1 per cent. solutions, and one cell in 2 per cent. solutions.				
			Exp. I.	Exp. II.	Exp. III.	Exp. IV.	Mean.
Chloride of potassium, 2 per cent....	9	2	6·58	6·79	6·82	......	6·73
Nitrate of soda, 2 per cent.	11·022	3	6·66	6·98	6·79	......	6·81
Chloride of sodium, 1 per cent. ...	11·022	3	6·33	6·63	6·73	7·06	6·69
Chloride of sodium, 2 per cent. ...	11·022	3	6·50	6·60	6·64	6·74	6·62
Sulphate of soda, 1 per cent.........	15·589	6	6·60	6·56	6·56	6·50	6·55
Sulphate of soda, 2 per cent.........	15·589	6	6·50	5·43	6·33	......	6·42
Sulphate of magnesia, 1 per cent....	25·456	16	6·36	6·20	6·86	6·59	6·50
Sulphate of magnesia, 2 per cent....	25·456	16	6·42	6·78	6·50	6·84	6·63

Several other salts were diffused in the same circumstances as the preceding, of which the diffusion products have been previously given. Of these salts, both the 1 and 2 per cent. solutions of nitrate of potash gave 6·83 in nine days, or in the same time as chloride of potassium in the table. The latter salt maintains a sensible equality of diffusion with the present series at the low, as well as it was found to do at the former high temperature. Chloride of sodium is here introduced for the first time: it appears to be equi-diffusive with nitrate of soda. If the sulphate of magnesia diffused be increased by 0·07, for its lower temperature, this salt will be in close accordance with the salts of potash and soda.

Taking nitrate of potash 6·83, as 100, for a standard, the salt which deviates most considerably is sulphate of soda, which for the 1 per cent. solution is 6·55, or 95·9. A low temperature, however, must be unfavourable to diffusion experiments, from increasing the tendency of salts to crystallize.

In conclusion, I may sum up the results of most interest which this inquiry respecting liquid diffusion has hitherto furnished.

1. I would place first the method of observing liquid diffusion. This method, although simple, appears to admit of sufficient exactness. It enables us to make a new class of observations which can be expressed in numbers, and of which a vast variety of substances may be the object, in fact everything soluble. Diffusion is also a property of a fundamental character, upon which other properties depend, like the volatility of substances; while the number of substances which are soluble and therefore diffusible, appears to be much greater than the number of volatile bodies.

2. The novel scale of Solution Densities, which are suggested by the different diffusibilities of salts, and to which alone, guided by the analogy of gaseous diffusion, we can refer these diffusibilities. Liquid diffusion thus supplies the densities of a new kind of molecules, but nothing more respecting them.

The fact that the relations in diffusion of different substances refer to equal weights of those substances, and not to their atomic weights or equivalents, is one which reaches to the very basis of molecular chemistry. The relation most frequently possessed is that of equality, the relation of all others most easily observed. In liquid diffusion we appear to deal no longer with chemical equivalents or the Daltonian atoms, but with masses even more simply related to each other in weight. Founding still upon the chemical atoms, we may suppose that they can group together in such numbers as to form new and larger molecules of equal weight for different substances, or if not of equal weight, of weights which appear to have a simple relation to each other. It is this new class of molecules which appear to play a part in solubility and liquid diffusion, and not the atoms of chemical combination.

3. The formation of classes of equi-diffusive substances. These classes are evidently often more comprehensive than the isomorphous groups, although I have reason to imagine that they sometimes divide such groups; that while the diffusion of salts of baryta and strontia, for instance, is similar, the diffusion of salts of lead may be different.

4. The separation of the whole salts (apparently) of potash and of soda into two divisions, the sulphate and nitrate groups, which must have a chemical significancy. The same division of the salts in question has been made by M. GERHARDT, on the ground that the nitrate class is monobasic and the sulphate class bibasic.

5. The application of liquid diffusion to the separation of mixed salts, in natural and in artificial operations.

6. The application of liquid diffusion to produce chemical decompositions.

7. The assistance which a knowledge of liquid diffusion will afford in the investigation of endosmose. When the diffusibility of the salts in a liquid is known, the compound effect presented in an endosmotic experiment may be analysed, and the true share of the membrane in the result be ascertained.

But on the mere threshold of so wide a subject as liquid diffusion, I must postpone speculation to the determination of new facts and the enlargement of my data, of the present incompleteness of which I am fully sensible.